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**DEVELOPMENT OF AN INNOVATIVE PYROLYSIS PLANT FOR THE
PRODUCTION OF SECONDARY RAW MATERIALS**

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Esame finale anno 2015

*To Maria Giulia and Maddalena,
For your daily smile*

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During the three years of her PhD, Chiara Leonardi has followed a project aimed at developing an environmentally and financially sustainable process to dispose of end of life tires. In this perspective an innovative static bed batch pilot reactor has been developed where pyrolysis can be carried out on the whole tires in order to recover energy and materials and simultaneously save the energy costs of their shredding. The innovative plant is also able to guarantee a high safety of the process thanks to the presence of a hydraulic guard. The main objective of this research was to evaluate the influence of the maximum process temperature on yields and chemical-physics properties of pyrolysis products. In addition, in view of a scale-up of the plant in continuous mode, the influence of the nature of several different tires as well as the effects of the aging on the final products were studied. Subsequently, the same pilot plant has been used to carry out pyrolysis on different types of waste such as polyethylene, biomass and polymer matrix reinforced composites (i.e, Carbon Fiber and Glass Fiber Reinforced Polymers). In the latter case, the pyrolysis process allows to obtain chemical feedstocks from the resin degradation together with the recovery of the reinforcement in the form of fibers. Carbon fibers reinforced composites and fibreglass was treated in the 450-600°C range and the products have been fully characterized. A second oxidative step was performed on the pyrolysis solid residue in order to obtain the fibers in a suitable condition for a subsequent reimpregnation in order to close the composite Life Cycle in a cradle-to-cradle approach.

These investigations demonstrated that pyrolysis-recovered reinforcements can be a viable alternative to pristine fibers. Steel wires, char, carbon and glass fibers recovered in the prototypal plant as solid residues out of the different batches have received positive evaluations as secondary raw materials by producers making use of them to obtain new products with a commercial added value. In this context, the candidate has proven to possess excellent ability to target-oriented work, both individually and in collaboration. She has learned to conduct medium-size experimental pilot plants, showing decision-making skills in different situations. She has consolidated the use of several experimental techniques and has acquired competences in comparing obtained data with current national and international regulations. In addition to scientific skills, the candidate has also shown a high predisposition for teamwork and interpersonal communications. During the three years of her PhD, the candidate has participated at several seminars, workshops and schools. The obtained results have been subject of eight oral or poster presentations, two scientific papers have been published in international journals and two are currently subject to peer-review. Taken into account the overall work carried out and the commitment proved, I express for the candidate the following judgment: excellent.

The Board expresses a score of excellence on the activity carried out by the candidate during the whole cycle of doctorate and considers her worthy to attain the PhD in Chemistry.

THESIS SUMMARY

This project was born with the aim of developing an environmentally and financially sustainable process to dispose of end of life tires. In this perspective was devised an innovative static bed batch pilot reactor where pyrolysis can be carried out on the whole tires in order to recover energy and materials and simultaneously save the energy costs of their shredding. The innovative plant is also able to guarantee a high safety of the process thanks to the presence of a hydraulic guard.

In this phase, the pilot plant was used to pyrolyze new and end of life tires at temperatures from 400 to 600°C with step of 50°C in presence of steam. The main objective of this research is to evaluate the influence of the maximum process temperature on yields and chemical-physics properties of pyrolysis products. In addition, in view of a scale-up of the plant in continuous mode, the influence of the nature of several different tires as well as the effects of the aging on the final products were studied.

Subsequently, the pilot plant was also used to carry out pyrolysis on polymer matrix composites in order to obtain chemical feedstocks from the resin degradation together with the recovery of the reinforcement in the form of fibers. Carbon fibers reinforced composites and fiberglass was treated in the 450-600°C range and the products were fully characterized. A second oxidative step was performed on the pyrolysis solid residue in order to obtain the fibers in a suitable condition for a subsequent re-impregnation in order to close the composite Life Cycle in a cradle-to-cradle approach.

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Steel wire, carbon char and carbon fiber recovered in the prototypal plant as solid residues of the different batches have received positive evaluations as secondary raw materials by producers making use of them to obtain new products with a commercial added value.

1. Introduction

1.1. Notion of secondary raw material and European regulatory framework on waste disposal

The notion of secondary raw material was first introduced by DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL [1], which has the purpose of moving the EU closer to a ‘recycling society’, seeking to avoid waste generation and using it instead as a resource. This Directive deals with the distinction between waste, by-product and secondary raw material, establishing the specifications within which a substance is subject to achieve a given qualification.

Article 3 of the DIRECTIVE 2008/98/EC defines the “waste” as any substance or object which the holder discards or intends to or is required to discard while Article 5 identifies the “by-product” as a “substance or object, resulting from a production process, the primary aim of which is not the production of that item”. To be considered a by-products, each substance must be produced as an integral part of a production process, and have a certain use without further treatment other than normal industrial practice.

For the purposes, key provision of the directive is Art. 6 entitled "End-of-waste status" that describes the requirements that allow a substance to lose the qualification of scrap or object to gain the status of so-called “secondary raw material”: “Certain specified waste shall cease to be waste (...) when it has undergone a recovery, including recycling operation and complies with specific criteria to be developed in accordance with the following conditions:

- the substance or object is commonly used for specific purposes;
- a market or demand exists for such a substance or object;
- the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products;
- the use of the substance or object will not lead to overall adverse environmental or human health impacts.”

Summarizing, subjecting disposable materials to recovery operations, it is possible to obtain products that, by meeting given requirements, can be used as raw materials.

The ‘recovery’ definition (Article 3) includes “any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfill that function, in

the plant or in the wider economy”. This definition includes the preparation for re-use and the recycling.

The regulations on waste management will apply until the material reaches the status of “end-of-waste”, is therefore crucial to clearly identify the transition from the status of waste to that of secondary raw material. The legal and judicial developments in the transposition of EU directives cannot be considered conclusive, nevertheless the DIRECTIVE 2008/98/EC paves the way towards waste valorisation and the development of the required technological processes to implement it.

The European waste management is diversified depending not only on the material itself, but also on the specific regulations on the disposal of items which they form. Nevertheless, all of the processes have to respond to European environment policy, which, since 1972, has developed into more than 200 Community legislation on the subject.

The EU Waste Framework Directive 2008/98/CE [1] provides the legislative framework for the collection, transportation, recovery and disposal of waste, and includes a common definition of waste. The directive requires all member states to take the necessary measures to ensure waste is recovered or disposed of without endangering human health or causing harm to the environment and includes permitting, registration and inspection requirements.

The directive also sets up a hierarchy for their disposal (Figure 1.1) and requires member states to take appropriate measures to first encourage the prevention or reduction of waste production and its harmfulness and secondly the recovery of waste by means of recycling, re-use or reclamation or any other process with the aim of extracting secondary raw materials, or the use of waste as a source of energy. The directive’s requirements are supplemented by other directives for specific waste streams. It is therefore necessary to deepen in the specific any valid rules about the disposal of the main materials of specific interest.



Figure 1.1 – Waste hierarchy

Those Directive are particularly challenging to address when the waste is a complex multimaterial object. The possibility of combining different types of components allows to modulate the properties of the composite according to specific needs: in this way it is possible to realize products that are able to at least bridge together the main properties of the single components in one material, and, in some cases, are able to outstand the mere sum of the components features attaining additional characteristics that arise from the synergical interaction of the individual constituents. On the contrary, it makes the separation of single phases at the end of life almost impossible precluding a virtuous disposal.

In this situation, the disposal of the end-life tires is a challenge for both the complexity of the materials which they are made, the great and growing amount involved and the regulatory limitations relating to their disposal.

But the above general description allows to insert in the classification wide range of materials and products thereof. Among them, Polymer Matrix Composites (PMCs) have established themselves as engineering structural material. This came about not only because of the introduction of high performance fibres such as carbon and aramid, but also because of some improved matrix materials.

The described features meant for a rapid development of the composites in application fields which today cover automotive, aerospace and defence, wind turbines, sport and leisure, in construction, boating and aeronautic industries, civil and industrial insulation, furniture and furnishings, special vehicles, insulation for ventilation equipment, structures for amusement rides, swimming pools, containers, structures for packaging and transporting, wind power, etc. On the other hand, composite materials are difficult to recycle due to the heterogeneous hybrid structure, difficult to part and thermoset composite materials are neither fusible nor soluble and are therefore considered even harder to recycle.

In particular, will be taken into consideration three types of composite materials, whose waste are characterized, due to specific laws or production chains, of high differentiation flows, namely tires, Carbon Fibers Reinforced Composites (CFRCs) and Glass Fibers Reinforced Composites (GFRCs).

In this frame the acquisition of technological skills allowing an added value recovery of wastes, instead of simply disposing of them, is a key enabling process in the implementation of the EU requirements. Those technological skills should be mainly addressed towards those kind of wastes that are presently considered components difficult to valorise as secondary raw materials, such as composites, owing to the intrinsic difficulty in separating components.

1.2. Tires

The tire is the component that covers the wheel's rim to protect it, enables better vehicle performance, provides traction between the vehicle and the road while providing a flexible cushion that absorbs shock.

1.2.1. Regulatory framework for disposal of end life tires

When the user decides to dismiss his vehicle's tires he relies on mechanical workshops or other equipped places, generally called "tire dealers", which have the task of determining if the dismissed tires have the characteristics to be reused or rebuilt. If there is no possibility of reuse, the tire becomes a "waste" as defined in Article 183 of Legislative Decree 152/2006 [2]. Hence the "end-life tire" (ELT) is a non-reusable tire in its original form and thus it enters a waste management system based on product/material recycling, and/or energy recovery.

The management of ELTs is becoming increasingly worrying owing to a number of concurrent factors such as the massive, and still growing, amount of exhausted tires involved (estimated annual world production of tires at 23.3 million tonnes [3]), the almost complete lack of biodegradability of such a kind of materials and the tendency to get rid of them wildly, with no concern at all about their destiny. Nevertheless, presently there are several available disposal techniques though each one presents some drawbacks

In Europe, the management of ELTs follows three main systems (Figure 1.2) [3]:

- liberal system (LS): the legislation sets the objectives to be met but does not designate any directly responsible subject. In this way all the operators participating in the recovery chain contract act under free market conditions and behave in compliance with legislation. This may be backed up by voluntary cooperation between companies to promote best practices;
- tax system (TS): under the tax system, each country is responsible for the recovery and recycling of the end of life tires. The goal is financed by a tax levied on (tire) production and subsequently passed on to the customer. This is a system whereby the producers pay a tax to the State, which is responsible overall for the organization and remunerates the operators acting in the recovery chain;
- producer responsibility (PR), the law defines the legal framework and assigns to the producers (tire manufacturers and importers) the responsibility to organize the management chain of end-life tires. This led to the setting-up of a non-profit organizations financed by tire producers aiming at managing collection and recovery

of end of life tires through the most economical solutions system with take-back obligation. At the EU level, they are grouped in ETRma.



Figure 1.2 – European ELTs management models in Europe [3]. ■ Producer responsibility system; ■ Liberal system; ■ government responsibility; ▲ Change of regulatory framework (on-going/under discussion) [3].

The Italian legislation, significantly evolved in recent years with the PR system introduction, describes ELTs as non-dangerous wastes labelled with 16 01 03 code number of the European waste list, "wastes from dismantling of end of life vehicles and vehicle maintenance."

Article 228 of 152/2006 Legislative Decree, Consolidated Environmental [2], gives manufacturers and importers of tires the obligation to ensure the management of ELTs in equal quantities to those placed for sale on the nationwide market. This obligation can be fulfilled both as an individual or as a group, and performances are checked at least annually. The same article also provides for the issuance of a ministerial decree regulating the system of Extended Producer Responsibility applied to the flow of the ELTs. Upon the issuance of the implementing decree 82/2011 [4], Ecopneus scpa was started up as a non-profit organization created by the major tire manufacturers operating in Italy: this consortium aims at tracing, collecting, treating and finally disposing of the ELTs. The recovery procedures through which

Ecopneus can operate are defined, in a simplified way, by the Ministerial Decree 05/02/1998 [5]. In particular with reference to:

- material recycling: for use in compounds; such as the production of bitumen or the realization of fenders (after appropriate treatment);
- energy recovery: the ELTs can be used in incineration for energy recovery only if they come as a fraction component of RDF (Refuse Derived Fuel) because of their chemical composition. In order to incinerate them as single-stream ordinary authorization system is required (Arts. 208-210, Legislative Decree 152/2006);
- insertion of ELTs in the list of recoverable waste by pyrolysis and gasification.

Legislative Decree 36/2003 [6], transposing Directive 1999/31/EC [7] on the landfill of waste, declares illegal the disposing of whole tires from 16/07/2003 and shredded ELTs from 16/07/2006.

1.2.2. Tire composition and structure

Though the size and structure of a tire may vary, depending on the vehicle on which is mounted, however it is generally composed of the structural parts described below.



Figure 1.3 - Radial structure of a tire.

As depicted in Figure 1.3, there are many different layers composing the tire, such as:

- Inner layer (1): consisting of halogenated butyl rubber, mainly chlorinated butyl rubber. It serves to prevent the leakage of air and moisture from the air zone (tubeless) to the tire carcass. Therefore it acts as a lining capable of maintaining the

internal pressure, also thanks to the addition of additives to improve chemical-physical properties and mechanical performances.

- Carcass (2): it is the backbone of the entire tire. It is composed of two layers of natural rubber (polyisoprene) interspersed with a layer of synthetic fiber, for example nylon, rayon or polyester. Tires for heavy cars or sports may have multiple layers of fiber.
- Low side (3): it is the padding material, capable of transmitting torque and the braking torque from the wheel rim to the contact area with the ground, the tread.
- Heel and belt (4): the heel is a layer of rubberized canvas that prevents the wear caused by the rubbing of the tire against the rim edge, and which ensures the necessary friction to prevent the rotation on the same. Embedded in the heel are the belts, high tensile strength round steel wires, often coated with special alloys of bronze or brass to act against corrosion. Belts are embedded in the rubber and form an inflexible and inelastic zone in the tire which serves to provide the best mechanical coupling with the rim.
- Side (or shoulder) (5): it consists of natural rubber (polyisoprene), often in blends with synthetic rubbers such as polybutadiene, to which are added antioxidants and antiozonants. Its function is to ensure that the tire structural characteristics are suitable for absorbing lateral impact energy.
- Belt plies (6): they are squares of rubber reinforced with steel wires very thin yet extremely strong, obliquely crossed and glued on each other. The intersection of these threads with those of the carcass deformable triangles, using a technique called triangulation ensures the stiffening of the top of the tire. In particular the plies must not stretch under the centrifugal effect and also be rigid in the transverse direction to resist the slip thrusts. The presence of rubber ensures an elastic behaviour in the vertical direction to overcome the obstacles. A very good adhesion between rubber and inorganic reinforcement is fundamental. According to their positioning with respect to the median axis, two types of tires can be distinguished:
 - diagonals: canvases extend diagonally from bead to bead of the tire forming an angle of 30-40° with the median line of the tire itself, where each canvas or subsequent layer of wire goes in the opposite direction and then crossing:
 - radials: canvases extending from one bead to the other with an angle of 90° with the median axis of the tire.

- Tread (7): is placed above the belt ply and is the part of the tire in contact with the road, according to the design of the grooves that there is engraved. The compound which composes it must ensure adhesion to all types of soil, high impact, wear and abrasion resistance and undergo a low heating for hysteresis and friction. This compound is mainly composed of SBR (Styrene-Butadiene Rubber), which guarantees stability against mineral oils, greases and hydrocarbons.

In the end, a tire is a complex object mainly composed of polymers of different nature, steel, inert fillers and additives. The average macro-composition of a cars tire can be summarized as in Table 1.1.

Table 1.1 - Average car tyre composition (wt%).

Rif.	Natural and synthetic rubber	Carbon black	Steel	Fibers and additives
[8]	58.8	27.7	9.6	3.9
[9]	27.6	27.6	9.6	3.5

The synthetic rubber materials most commonly applied in tires are SBR, polybutadiene and chloro-butyl rubber, while for natural rubber there is polyisoprene. The fibers used in the production of tires are made of nylon, rayon and polyester. The carbon black appears as an amorphous black carbon powder, obtained as a byproduct of incomplete combustion of any organic substance: it constitutes a high portion of the rubber, providing reinforcement, color and resistance to degradation. Part of the carbon black can be replaced with silica, which is used to reduce the rolling resistance and improve grip on wet roads. Consequently, silica is mostly present in the thermal winter tyres because responsible for the reduction of the heating time of the rubber. The additives commonly added to the mix are:

- activators of vulcanization: zinc oxide or, alternatively, fatty acids such as stearic acid.
- Vulcanizing agents: sulfur or sulfur donors. They make up about 3% by weight of the rubber fraction (net of steel) Rubber vulcanization is required to provide resistance to the rubber through the formation of disulfide bonds (crosslinks) between macromolecules, providing a dense infinite 3D network.
- Accelerators of vulcanization: organic complexes that accelerate the reaction of rubber vulcanization such as hexamethylenetetramine, thiazoles, sulphenamides, thiuram and dithiocarbamates;

- antioxidants and antiozonants: they are used to prevent the molecular cracking reactions caused by the action of sunlight and ozone, especially along the sides of the tire, which are more exposed to direct sunlight. For this purpose, p-phenylenediamines are generally used.

1.2.3. Recovery of end-life tires

As previously discussed, a tire is considered at its “end of life” only if it cannot be rebuilt. Since landfilling ELTs is prohibited, the pathways for waste tires management are necessarily going through materials and/or energy recovery.

Materials recovery from whole ELTs can be achieved via production of sound barriers and/or anti-erosion panels to be applied in road embankments and coastal defences. Otherwise, ELTs can be recovered after a cracking and/or grounding process (at room temperature or in cryogenic conditions with liquid nitrogen) in forms of chips, granules or dusts. However, the crushing operation involves a significant energy consumption, though it also attains the separation of the rubber from steel and the textile part, thus optimizing the recovery of each type of material. The crushed ELTs are used in the steel industry as a partial replacement of anthracite and coke used as reducing agents of the metal oxides. The rubber powder is used for the production of asphalt or surfaces with special elastic characteristics. Moreover, the powder can be used in the formulation of compounds for new tires. Finally, if admixed with polyurethane resins they can be used for the realization of materials for the insulation, for the urban furniture and for mulching. In recent years there has been finally the reuse of ELTs for the production of accessories, shoes, design objects, works of art.

On the other hand, tires are excellent fuels, they have a calorific value of about 32-40 MJ/kg [9-11] which is comparable to that of pet coke or coal of excellent quality. Therefore, tires are used for energy recovery (mainly co-incineration) in energy-intensive industrial installations, such as cement kilns, paper, etc. With respect to common fuels, incinerating tires involves the development of non-fossil CO₂. However, this solution leads to the loss of valuable materials and the production of polluting emissions, thus imposing expensive gas cleaning devices.

Presently, 49% of ELTs managed in countries where there is the responsibility of the manufacturer is treated with an aim to material recovery, as can be seen in Figure 1.4. When used for energy recovery, ELTs are mainly applied (86%) in cement kilns [3].

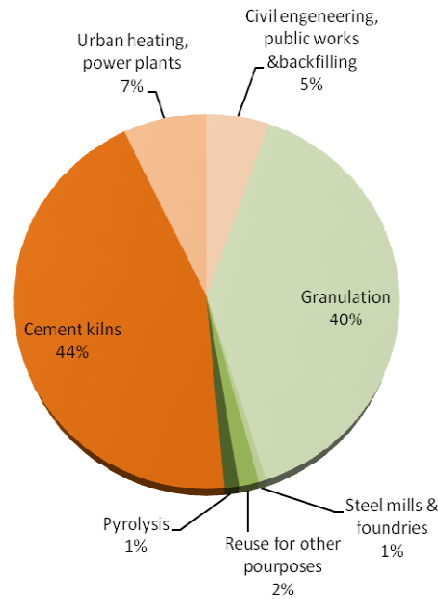


Figure 1.4 – ELTs management in ETRma network in 2013. Orange: energy recovery, Green: material recovery.

Among the available disposal techniques, pyrolysis of tires has received renewed interest because it has the advantage to be considered both a material and an energy recovery approach. Furthermore, the treatment in the absence of oxygen prevents the formation of chemical species with high environmental impact typical of incineration processes.

1.3. Fiber reinforced Polymers (FRPs)

Fiber reinforced polymer composites consist of fibers of high strength and high modulus embedded in a polymer matrix. In the composites, fiber and polymer both maintain their original physical and chemical characteristics. The composite they produce has combined mechanical properties which are somehow different than either component acting alone. In the composite, fiber is the load-carrying component and the main source of strength while the matrix “glues” all fibers together in position, acts as a load transfer medium between them, and protects fibers from environmental damages.

The use of fibers as high-performance engineering materials is based on three characteristics:

- Size effect: the small diameter with respect to its grain size or other microstructural unit allows a higher fraction of theoretical strength compared to that obtainable in the bulk form;
- High aspect ratio: the high length/diameter ratio allows a very large fraction of the applied load to be transferred via the matrix to the stiff and strong fiber;

- Flexibility: the high degree of flexibility is a characteristic of a materials that has a high modulus and a small diameter [12].

Table 1.2 – Properties of selected commercial reinforcing fibers [13].

Fiber	Density (g/cm³)	Modulus (GPa)	Tensile Strength (GPa)	Strain-to- failure (%)
E-Glass	2.54	72.4	3.45	4.8
T-300 (PAN carbon)	1.76	231	3.65	1.4
P-55 (Pitch carbon)	2.0	308	1.90	0.5
P-100 (Pich carbon)	2.15	758	2.41	0.32
Kevlar49 (Aramid)	1.45	131	3.62	2.8
Boron	2.7	393	3.1	0.79
SiC monofilament	3.08	400	3.44	0.86
Nextel 610 (Al ₂ O ₃)	3.9	380	3.1	-

The most common fibers used in advanced composites for structural applications are glass, aramid, and carbon fibers. Other fibers, such as boron, silicon carbide, and aluminium oxide, are used in limited quantities [13]. Properties of selected commercial reinforcing fibers are listed in Table 1.2.

1.3.1. Carbon Fibers Reinforced Compounds (CFRCs)

Carbon Fibers (CFs) are used in an increasing number of sectors, such as automotive, aerospace and defence, wind turbines, sport and leisure, owing to their impressive mechanical properties associated with light weight. Over 97% of the CFs are used as reinforcement in composite materials and a large part of them (95%) is processed in a plastic matrix for production of Carbon Fiber Reinforced Composites (CFRCs) [14].

Carbon fibers are very strong and thin and they are usually obtained by the controlled pyrolysis of synthetic fibers. Carbons in the fiber have a structural similar to that of graphite where atoms are arranged in a hexagonal array along flat planes. There is a high degree of strength across the planar direction of this structure due to the strong sp^2 carbon to carbon bonding. In carbon fiber these sheets are long and thin, and they are usually referred to as ribbons. Unlike graphite, carbon fiber has less long range ordering and the ribbons of carbon atoms are aligned parallel to the axis of the fiber. Within the inner portions of the carbon fiber the ribbons of carbon atoms fold over onto one another in a “hairpin” fashion.

The interconnection of carbon sheets is believed to give carbon fiber its incredible mechanical properties. Carbon fibers were first commercially made by Thomas Edison, who during his research in 1879 carbonized cotton and bamboo fibers in order to use them as filaments in his incandescent light bulbs. Since then, manufactures have made great strides in the field of carbon fiber production technology. Today carbon fibers are typically prepared from polymeric precursor materials, such as polyacrylonitrile (PAN), cellulose, polyvinylchloride, and from pitch. PAN-based and PITCH-based carbon fibers are predominately used to create high strength, high modulus fibers used in structural and aerospace applications. PAN-based carbon fibers will be the primary carbon fiber focused on in the research presented during this report.

The manufacturing process of converting PAN into carbon fibers is typically accomplished in a continuous four step process. This four stage process consists of:

- oxidation: involves heating the PAN fibers up to 300°C in an air rich environment in order to alter the PAN atoms arrangement from a ladder-like to a ring-like structure and also to replace elemental hydrogen with oxygen (Figure1.5). During this thermoxidative step the fibers reach a stabilized structure that helps them to withstand the subsequent high-temperature treatments and also changes their color from white to brown, then to black.

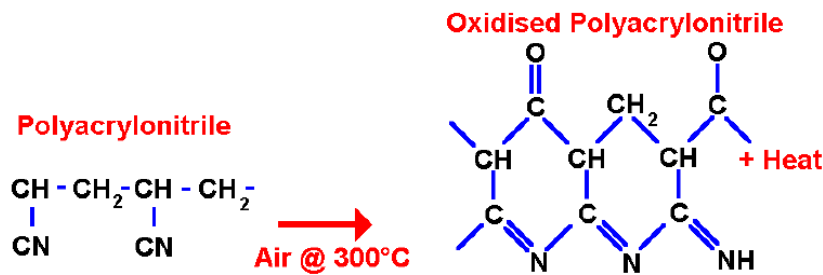


Figure 1.5 – Oxidation of PAN precursor [15].

- Carbonization (Figure 1.6) and graphitization: these high temperature treatments (carbonization at 1600°C and graphitization >2000°C) are performed in order to exclude the noncarbon atoms from the structure. They attain a structurally ordered carbon arrangement, improving the orientation of the basal planes and adding stiffness to the fibers.

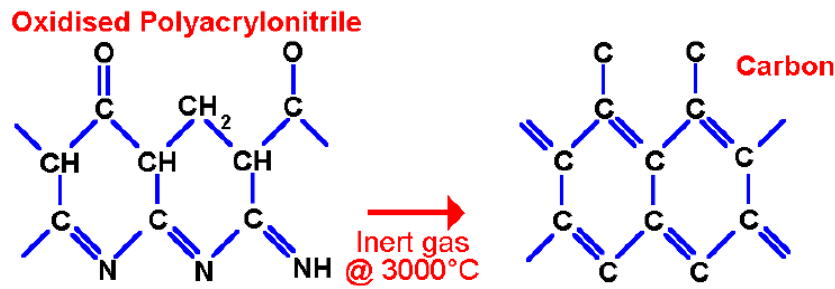


Fig. 1.6 – Carbonisation of oxydized PAN [15].

- Surface treatment: after carbonization, the carbon fibers are ready for surface treatment, that modifies the surface of the fibers for maximum adhesion between the fibers and the polymer matrix. This fiber treatment is an important factor in the production of carbon fibers that are intended for use in polymer matrices where the strength properties of the finished composite is directly related to the fiber to matrix adhesion. The interface between these carbon fibers and their subsequent matrix is a key component in the transfer of stress from the matrix to the higher modulus load bearing fibers. There are a variety of batch and continuous surface treatment processes used to obtain desirable carbon fiber surface properties, these include oxidative and non-oxidative methods. Oxidative methods include gaseous, solution, electrochemical, plasma and catalytic processes. Non-oxidative methods include the deposition of an active form of carbon, the deposition of pyrolytic carbon and the grafting of a polymer onto the fiber surface.
- Sizing: the final carbon fiber processing step is the application of a sizing agent. This sizing is typically a polymer coating applied to the fibers which aids in inter-filamentary adhesion, promoting fiber wettability in the resin matrix, and protects the fibers during further processing. The most common method for applying sizing to carbon fibers is continuous deposition from solution of a polymer. Other sizing application methods used are deposition of a polymer onto the fiber surface by electrodeposition, plasma polymerization, and deposition of a polymer via electropolymerization [15].

There are a number of methods used to introduce carbon fiber into a resin matrix to create high performance carbon fiber composites, such as pultrusion, vacuum molding, filament winding and laminated composite. The latter starts from prepregs, which are rolls of sheets of unidirectionally oriented CFs or woven fabrics, preimpregnated with a partially cured resin matrix. The resin is then no longer in a low-viscosity stage, but it has been advanced to a

B-stage level of cure for a better handling characteristics. In order to make them commercially available, removable backing sheets are used to prevent sticking of the layers.

The prepreg technology is one of the most commonly applied in the composite production, that in this case involves the cutting of the prepregs in the required shapes to lay up the artefact. In this stage the prepregs waste production may vary up to 45%wt, according to the design of the object (shape, size and orientation of the fibers) and the ability to optimize the available material.

According to the design plan of the artefact, the sheets of cutted prepreg are formed individually or stacked in layers until reaching a thickness of several centimetres. Otherwise, for structural profiles produced for use in the construction industry for building and bridge superstructure applications, [16] or for advanced uses, the prepreg sheets can be assembled in a sandwich structural form. In the last case, two or more prepregs are disposed in parallel face sheets bonded to and separated by a relatively thick, lightweight core. The core supports the sheets against buckling and resists out-of-plane shear loads. The core must have high shear strength and compression stiffness [18].

After the complete curing of the resin, the product is trimmed and generally subjected to a quality control attesting to match the specifications. These stages give rise to cured materials cut-offs with different geometries and dimensions that are considered as waste. The amount of waste generated in this case is closely related to the geometry of the object, and in the end, to the overall optimization of the production process.

1.3.2. Glass Fibers Reinforced Compounds (GFRCs)

Glass fibers are the most widely used reinforcing fibers due to their low cost, high tensile strength, high chemical resistance, and excellent insulating properties.

Glass fiber reinforced compounds (GFRCs) are composite materials widely used in construction, automotive, boating and aeronautic industries. The composite nature and the cross-linked matrices give rise to materials that cover a wide range of mechanical, chemical and physical properties.

GFRCs polyester resin laminates are extremely versatile and ideal for use in various fields of application, such as, among the most important ones, nautical, trains, civil and industrial insulation, furniture and furnishings, special vehicles, insulation for ventilation equipment, structures for amusement rides, swimming pools, containers, structures for packaging and transporting, wind power, etc.

Within the “glass fiber” category there are further subdivisions. Table 1.3 gives the composition of some types of glass currently available which are applied in Fiber Reinforced Polymers (FRPs). The type of glass commonly used for reinforcing is the E-glass type, where “E” stands for “electrical” because E-Glass is a good electrical insulator in addition to having good strength and a reasonable Young’s Modulus [13]. E-glass is the material of choice in several applications such as FRP wrap systems because of its low cost compared to the alternative available [15]. In C-Glass “C” stands for “Corrosion” because it has a better resistance to chemical corrosion; while in S-Glass “S” is correlated to the high silica content that makes it able to withstand higher temperature than other glasses [12].

As shown in Table 1.3, the predominant molecular unit in all the glass fibres is silicon oxide. Silicon oxide is what gives the glass fibres their strength but at the same time can be their weakness since it is prone to undergo chemical reactions involving basic hydroxyl ions. These reactions deteriorate the fibre matrix which in turn may degrade significantly the internal structure of the fiber.

Tabella 1.3 – Approximate chemical composition and properties of various glass types [12, 19].

	E-Glass	S-Glass	C-Glass	ECR-Glass	AR-Glass
Component (%)					
Ref.	[12]	[12]	[12]	[19]	[19]
SiO ₂	55.2	65.0	65.0	54-62	62
Al ₂ O ₃	8.0	25.0	4.0	12-13	-
CaO	18.7	-	14.0	21	5-9
MgO	4.6	10.0	3.0	4.5	1-4
B ₂ O ₃	7.3	-	5.0	<0.1	<0.5
K ₂ O	0.2	-	-	0.6	-
Na ₂ O	0.3	0.3	8.5	-	12-15
ZrO ₂	-	-	-	-	17
Properties					
Ref.	[19]	[19]	[19]	[19]	[19]
Density (g/cm ³)	2.6	2.53	2.52	2.72	2.68
Tensile Strength (GPa)	3.4	4.4	2.4	3.44	3.0
Strain-to-failure (%)	<4.8	<4.6	<4.8	<4.8	<4.4
Thermal coefficient (x10 ⁻⁶ /°C)	5.0	4.0	6.3	5.9	6.5
Softening temperature (°C)	850	980	750	880	770

The primary component of glass fiber is sand, but it also includes varying quantities of feldspar, sodium sulfate, anhydrous borax, boric acid, and many other materials.

On the basis of the composition, the raw materials are weighted and melted in a hopper and the molten glass is fed into the electrically heated platinum bushing or crucibles; each bushing contains about 200 holes at its base. The molten glass flows by gravity through these holes, forming fine continuous filaments; these are gathered together into a strand and a size is applied before it is wound on a drum [13]. On the basis of the composition, the raw materials are weighted and melted in a hopper and the molten glass is fed into the electrically heated platinum bushing or crucibles; each bushing contains about 200 holes at its base. The molten glass flows by gravity through these holes, forming fine continuous filaments; these are gathered together into a strand and a sizing treatment is applied before it is wound on a drum [13].

The main composite production manufacturing processes are pultrusion, where the reinforcement glass fibers are impregnated with resin (binder), and pulled through a heated stationary die for making constant structural shapes; gun roving, a spray-up process where a continuous roving strand is fed into a chopper gun that chops the strands into short lengths and deposits the fiber into a resin spray pattern for application on the mold surface: in this way, the wet glass laminate is created in situ from the spray gun; filament winding, which involves the winding of continuous fibers impregnated with resin on the rotating spindle along a defined path; compression moulding, in which the artefact is inserted in a mould and formed by compression with a counterpart [12, 19].

The limited intrinsic difficulties of the production process allows the production of large-size artefacts. The production process leads to cured resin scraps resulting from the trimming processes.

1.3.3. Recovery of GFRCs and CFRCs

Glass fibers reinforced Compounds (GFRCs), commonly named fiberglass, and Carbon Fibers Reinforced Compounds (CFRCs), both as end of life products and as production waste, are not subject to special regulations for their disposal other than those for the common of waste. In this framework, April 3, 2006 Decree n. 152 (Consolidated environmental) [2] is of particular interest. However, an exception is made for the disposal of fiberglass boats that need specific regulations due to the high occupied volumes and to the high numbers of concerned floating vehicles (27000 units with an average weight of 1.37 tons [20]).

Currently, the proper disposal of vessels for demolition includes reclamation and securing the site (manual operation of dismantling, separation of parts of the boat and recovery of recyclable fractions); tear the hull down and separating the fiberglass part and provision of in landfills of the non-recoverable fraction. Despite this, the sinking of vessels erased from the register of boating is illegal though currently practiced.

The “composite” nature and the predominantly cross-linked matrices used are what makes these materials difficult to recycle. Thermoset composite materials are neither fusible nor soluble and therefore it is not possible their re-use via reshaping. Nowadays, the main recycling methods applied to this type of composites could be classified in two types: a) mechanical recycling and b) fibers recovery through thermal or chemical processing [21]. The mechanical approach allows the recovery of composites by breaking them down, without any components separation, via mechanical processes like shredding, crushing or milling; the powdered product can then be used in low-value applications, primarily as fillers or particle reinforcements [22]. Though in this way a new life can be given to the composite, a recycling process which is able to give back fibers that can re-enter into production processes looks far more attractive, allowing a Cradle to Cradle approach that virtuously closes the Life Cycle of the material. Both chemical and thermal recovery, of which pyrolysis is an example, involve the decomposition of the polymeric component, allowing the re-use of the carbon fibers with good mechanical properties in the production of new polymeric composites such as short fiber reinforced composites and Sheet Molding Compounds (SMC). Chemical recycling methods are based on the application of reactive media which are able to decompose the polymeric fraction even in mild conditions: this approach, however, is generally characterized by a low tolerability against contaminants and a low industrial scalability, since it has a high environmental impact risk if hazardous solvents and reactants are used [21]. Recently, taking into account environmental issues, Liu et al. recycled CFs from epoxy CFRC in supercritical water in the presence of phenol and KOH [23]. They found that oxidant species can promote the decomposition of epoxy resin and that the recovered carbon fibers were not damaged during the recycling process.

On the other hand, thermal recovery is generally characterized by high energy consumption. Moreover, depending on the applied conditions, such as incomplete oxygen deprivation as in the pyrolysis, a smooth layer of pyrolytic carbon can lay down on the fibers [24]. Alternatively, thermal degradation might also occur in an oxidizing environment: in this situation the resin phase decomposes to valueless products [25], while the process leaves the

fibers clean from any carbonaceous residue but converts hydroxyl groups into a higher oxidation state [26].

In recent years, several studies concerning the recycling of GFPs and CFRCs have demonstrated the benefits brought by the pyrolysis process which involves the degradation of the organic components allowing the recovery of the fibrous reinforcement in suitable conditions to be re-used [13, 27-29]. Moreover, a pyrolysis plant presents several advantages in comparison with other thermo-chemical process plants, as depth in the next chapter [30, 31]. In recent years, several studies concerning the recycling of GFPs and CFRCs have demonstrated the benefits brought by the pyrolysis process which involves the degradation of the organic components allowing the recovery of the fibrous reinforcement in suitable conditions to be re-used [13, 27-29]. Moreover, a pyrolysis plant presents several advantages in comparison with other thermo-chemical process plants, as discussed in hereafter [30, 31].

Reports from industry suggest that using pyrolysis to recover CF from CFRP waste will consume only 5–10% of the energy required to produce Virgin Carbon Fibre (VCF) from their precursors. However, while this implies that benefits can exist, an assessment of environmental performance must extend beyond the simple energy consumption required for the material recovery process. Benefits from recycling might also arise when a material is successfully reintroduced into a secondary product system. When the latter is the case, i.e. a virgin material has been replaced by an analogous from a recycling processes, the environmental burdens related to the virgin material production are thus avoided together with those associated to the disposal of the waste material would have been disposed of [32].

1.4. Pyrolysis and pyrolytic products

Pyrolysis, also named thermolysis, thermal distillation, thermal depolymerisation, polymer cracking or reverse polymerisation, has been used to produce charcoal from wood and solid and gaseous fuel from coal and biomasses. Nowadays it's analytically applied in the preparation of complex samples and industrially for the production of carbon fibers from polyacrylonitrile. More recently it has been used for treating plastic wastes [24, 33], municipal solid wastes (MSW) [30] and for end-life tires disposal (ELTs) [34, 35].

With respect to other thermo-chemical processes, pyrolysis seems to be more attractive because presents several advantages:

- it can be run in adaptable capacity;

- it requires smaller off-gases cleaning system thanks to the low amounts of oxides produced as a consequence of the inert atmosphere;
- may reduce and avoid corrosive emissions by retaining alkali and heavy metals within the process residue;
- reduces PAHs generation in comparison with direct combustion;
- lower process emissions from pyrolysis units with minimal air pollution impacts because the greatest part of the pyrolytically generated gases is burned as a fuel in the process;
- the products are generally easily manageable and then exploitable separately, according to different final objectives;
- the use of products as a secondary raw materials allow a remarkable CO₂ emission reduction.

On the other hand, one noteworthy problem consists on the efficient and homogeneous heat transfer required to drive the pyrolysis process in such a way that the temperature is evenly distributed. Another important disadvantage is linked with legislative barriers because any plant dedicated to thermal treatment of wastes, regardless of any possible heat recovery, is still considered as incineration. Finally, some authors point out that owing to the absence of a wide market for the pyrolysis products, this process would never spread at industrial level [34].

The thermal degradation at high temperature leads to thermal cracking of the polymer chains of the matrix leaving substantially unaltered the reinforcements. Pyrolytic products depend on the treated waste but can be summarized in four main streams not necessarily always contemporary present (Figure 1.7): a partially condensable gaseous fraction and an oily phase that comes from condensed volatile fractions that can both be used as a fuel or chemical feedstocks, and a solid residue, generally composed of a carbonaceous residue, inorganic fillers and/or reinforcement in case of composites materials [36].

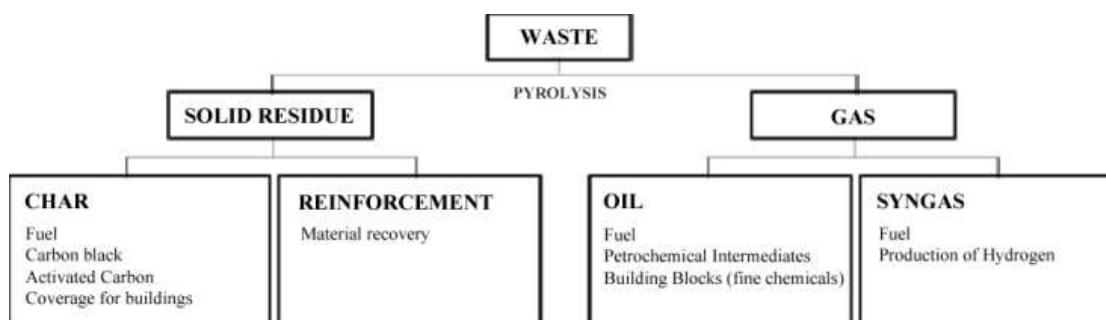


Figure 1.7 - General scheme of the subdivision of the pyrolysis products of polymer matrix composites.

The yields of the products and their composition is different depending on the type of matrix, but the main pyrolysis products are substantially similar for all polymer based treated waste:

- Char: it has been reported [28] that a certain amount of char, or coke-like material, is formed during the pyrolysis of many polymeric materials due to secondary repolymerisation reactions in the gaseous phase. It is a compound largely composed of amorphous carbon, the presence of other elements is strongly related to the composition of the polymer matrix and the use of fillers and additives [37-39]. The ability and convenience of retrieving the char is related to the amount produced. The char obtained from the pyrolysis of tires is composed of the sum of the carbon black already included in the tire formulation and what is formed by the thermal degradation of the organic matrix. The high yields and its Gross Calorific Value (GCV), of about 28.8 MJ/kg [8], makes it a good candidate as a fuel. Moreover, some activation studies were conducted in order to increase its surface area, so that recovered char can be used as a secondary raw materials for carbon black, active carbon [40] or as additive in road bitumen [41]. The pyrolysis of fiberglass and CFRCs leads to the formation of small quantity of carbonaceous residue, which homogeneously covers the fibers in a thin layer [28]. In these cases, the char is difficult to retrieve to be used as feedstock, and must be instead removed in order to obtain fibers in suitable conditions to be reused.
- Oil fraction: it is the condensable fraction of the volatile degradation products of the organic component. It is a mixture of organic compounds and an aqueous phase, with a variable composition depending on the type of process (loaded waste, temperature, pressure, and duration of the process). In any case it contains hydrocarbons of medium to high molecular weight, cyclic and aromatic compounds [28, 41] as well as, in the case of oil derived from the pyrolysis of tires, sulfur compounds [11]. The pyrolytic oil, once separated from the aqueous phase, may be directly used as fuel or subjected to distillation: the lighter fractions can be used as a source of high value chemicals such as benzene, toluene and xylene (BTX) and limonene and as extender oil in rubber formulation; the heavier fractions have been tested as additives in road bitumen and as feedstock for the production of coke. Potential end-uses for the pyrolytic oil in the petroleum refining industry include its use as oil feedstock for the fluid catalytic cracking (FCC) process in order to produce light fuels, for the thermal

cracking process in order to produce light products and olefin rich gases, and for the delayed coking process in order to produce light products and coke [42].

- Syngas fraction: the non-condensable gaseous fraction is a fuel gas mainly composed of H₂, CH₄ and short chain hydrocarbons (up to C₄/C₅). There are also CO, CO₂ [43] and, in the case of syngas derived from the pyrolysis of tires, H₂S [8] due to the presence of sulfur used for the vulcanization of the tires. It can be used primarily as a fuel, thanks to its high calorific value (of about 42 MJ/kg [8]), but some authors [44] propose the maximization of yield in hydrogen fraction to be applied for energy systems.

1.5. State of art of industrial pyrolysis reactor systems

Pyrolysis of waste tires has been widely developed throughout the world but it's currently restricted to a limited scale and mainly for research purposes. In this context, different technologies have been applied to tires pyrolysis: the process can be performed with or without a catalyst in order to maximize the yields in interesting volatile products [45] and a number of different reactors can be used, such as conical spouted bed reactor [39], autoclaves [8, 9] circulating fluid bed reactor [46], fixed bed reactor [47], rotating cone, tubing bomb reactors, free fall [34, 35] and high vacuum process [42]. All these reactors/configurations have advantages and disadvantages in terms of technical, economic and ecological parameters and are used for different energy applications such as distributed generation (heat and/or electricity) and/or the production of liquid fuel or secondary raw material from char.

The disposal of fiberglass by pyrolysis is not deeply studied nor industrially applied. This situation is due to the low value of the glass fibers, limiting profit margins of the process, but it is also especially due to the current lack of regulation regarding the disposal of large products, such as boat hulls.

Contrary to the development of the pyrolysis of tires, the study of the pyrolysis process of CFRCs has mainly focused on the possible reuse of the fibers and, in recent years, have been successfully launched the first industrial processes. A list, certainly not exhaustive, of companies that offer recovery services of CFRCs by pyrolysis includes are reported in Table 1.4 [48].

Introduction

Table 1.4 – Commercial and near commercial composites recycling service [48].

Company - location	Materials recycled	Process/capacity	Recyclate market	Website
Commercial				
CFK Valley Stade Recycling GmbH & carboNXT GmbH Stade, Germany	All kinds of CFRP waste materials	Pyrolysis, >1000 tonnes/year, launched in 2011	Milled 80-500 µm. Fibreball/pelletised/chopped 1-100 mm (e.g. for PA, PC, PP reinforced compounds). Wet laid veil 10-30 g/ m ² (e.g. for surface optimisation, EMI shielding). Air laid nonwovens 200-600 g/m ² (e.g. for RTM process for structural parts, SMC & BMC process).	www.carbonxt.de http://cfk-recycling.com
ELG Carbon Fibre, West Midlands, UK	Dry carbon fibre waste, carbon fibre prepreg waste, carbon fibre laminates	Pyrolysis process, 2000 tonnes/year recovered carbon fibre output	Chopped/milled/pelletised carbon fibre. Carbon fibre random mats and discontinuous fibre yarns. Preforms.	www.elgcf.com
Materials Innovation Technologies – Reengineered Carbon Fiber (MIT-RCF), South Carolina, USA	All kinds of CFRP waste materials	Pyrolysis, current capacity 2000 tonnes/ year recovered carbon fibre output (room for expansion)	Nonwoven rolled goods. Chopped fibre for compounding and long fibre reinforced thermoplastic (LFT) applications. Preforms (3-DEP™ process).	http://mitrcf.com
Reprocover, Belgium	Thermosets, including GRP with or without fibre reinforcement. Dry glass fibre waste	Thermoset waste ground to max. 6 mm granules. 30% glass fibre flakes mixed with 70% thermoset granules, resin added, high pressure cold moulded.	Utility boxes, rail infrastructure products (e.g. cable tray covers), flower boxes, bins etc.	www.reprocover.com
Zajons Logistik, Melbeck, nr. Hamburg, Germany	Cured GRP 100% recovery guarantee (thermal recovery/ recycling)	Comprocycle process. Shredded and mixed with RDF (refuse derived fuel) for use in cement kilns. Capacity 60,000 tonnes/year.	Used in Holcim cement kilns. Mineral content of glass and filler becomes cement feedstock, polymer content is burnt for calorific value.	www.comprocycle.com
Procotex, Dottignies, Belgium, and Apply Carbon, Languidic, France	Dry fibres: carbon, aramid, PEEK and natural fibres etc.	Pulling, garneting, carding, drying, milling, precision cutting to length. Sizing of chopped fibre available from autumn 2014.	Milled (from 75 µm) and cut carbon up to 120 mm. Various natural fibre products. Aramids, cut 0.25 to 120 mm. Pulled fibres and carded tows. Various other technical fibres pulled/cut.	http://en.procotex.com

Introduction

Company - location	Materials recycled	Process/capacity	Recyclate market	Website
Near commercial				
Extreme EcoSolutions , Netherlands	Cured GRP including whole products (e.g. boats)	---	Have started collecting production and end of life waste, working with selected partners in the transport and dismantling sector. The intention is to shred the GRP and grind to powder. This would be transported to Norway for recycling, initially as an additive for polyethylene film products in a process which is under development.	http://extremeecosolutions.com
Carbon Fibre Recycle Industry Co Ltd, Japan	CFRP waste	---	Utilising thermal decomposition by self-combustion process (6.7 MJ/kg-CF, 13.2 MJ/kg-CF), the company expects a recycling output of 1080 tonnes/year.	http://698.jp/cfri
Global Composites Recycling Solutions, UK	Cured GRP and glass fibre	---	Ground GRP and glass fibre is incorporated with other materials into Ecopolycrete. This is to be sold as a mix for polymer concrete type applications which can be precast or poured in place for railway sleepers, parking stops and other construction products. The material has a steel-like compressive strength and very high fire resistance. Expected to go commercial in Tennessee, USA, from September 2014, and soon afterwards in Northamptonshire, UK	www.ecopolycrete.com
Hambleside Danelaw, UK	Cured GRP	---	Have developed a process for mechanically recycling GRP to retain fibre length. These fibres have been utilised to form reinforcements both as chopped fibre and in nonwoven recycled fibre mats. The fibres have been used in both thermoset and thermoplastic composites to form products for the construction industry. Experimentation has also been carried out in using the fibres with concrete and with rubber to enhance the properties of these materials.	www.hamblesidedanelaw.co.uk
Karborek RCF, Puglia, Italy	CFRP waste	---	Pyrolysis process with energy recovery, to produce chopped/milled carbon fibres and carbon fibre felt. Capacity up to 1500 tonnes/year. The plant will be completed in October 2014, expecting to be in production from January 2015.	www.karborekrcf.it

Three of the company listed in Table 1.4 offer pyrolysis recycling process:

- CFK Valley Stade Recycling GmbH & Co KG [49], which has launched in 2011 a pyrolysis plant which work with a minimum capacity of 1000 tonnes/year. The plant, located in Wischhafen, Germany, produces chopped (1-100 mm) and milled (80-500 µm) carbon fibers. The process involves:
 - Presorting: crushing and sorting of materials according to type of fiber and state of processing: dry carbon fiber scraps, prepreg materials, end-of-life parts;
 - Pyrolysis: in order to recover pure carbon fibers completely by means of thermal oxidation of pyrolysis gases;
 - Refinement: customized conditioning of fiber surface;
 - Cutting: processing of carbon fibers into models "chopped" and "milled" - accurately cut to desired fiber length;
 - Customization: customization of the product on the basis of the requirements [49].
- ELG Carbon Fibre [50] recycles dry fibers, prepregs and laminate in a 2000 tonnes/year pyrolysis plant, located in West Midlands, UK. They offer a wide range of products as a result of a stepwise process which involves (Figure 1.8) shredding, thermal decomposition in absence of oxygen and chopping.

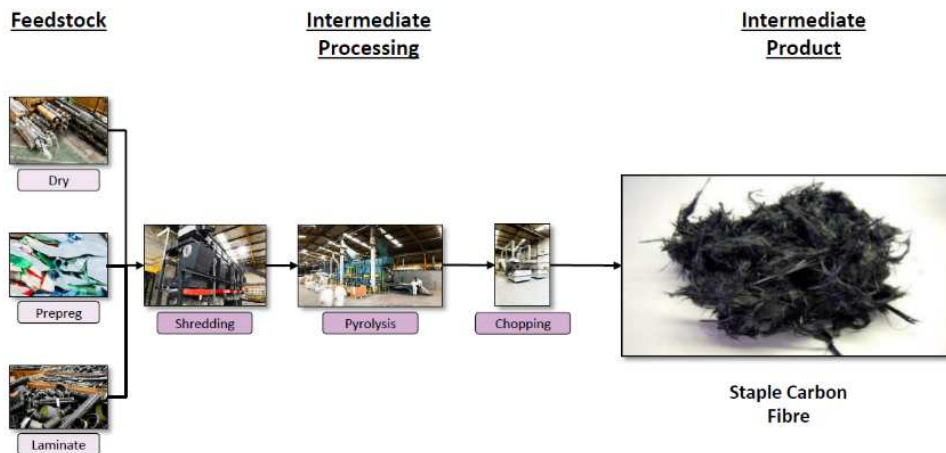


Figure 1.8 – Stepwise process applied by ELG Carbon Fibre on CFRCs wastes [50].

- MIT-RCF [51] recycles all kind of CFRCs wastes in a 2000 tonnes/year pyrolysis plant and offers a 3-DEPT™ molding process, providing an opportunity to manufacture sustainable parts with reclaimed carbon fibers [51].

1.6. Main pyrolysis reactor

Among the several configurations available and applied to the pyrolysis of different types of waste, the most studied include fixed bed reactors, rotary kiln, fluidized-bed reactors and tubular reactors. The characteristics of the reactor have a significant influence on the the pyrolysis outcomes.

In particular fixed bed reactors are characterized by low heating rate, as result of the low heating transfer coefficient. Therefore, when a significant sample mass is treated, the temperature is not uniform along the sample and, as a consequence, it is decomposed simultaneously at different temperatures. For this reason, this type of reactor are scarcely applied for pyrolysis at industrial level, finding their preferential use in the identification of those parameters affecting pyrolysis products and in scale-up processes.

In rotary kiln reactors, the slow rotation and the inclination of the kiln enable a good mixing of the wastes. This results in an improved homogeneity of the sample, crucial when processing a flow of mixed wastes, and in a greater efficiency in heating up the feedstock, if compared to fixed bed reactors. On the other hand, during pyrolysis, only the reactor wall serves to transfer heat to the treated mass. The small wall surface requires a low heating rate and, therefore, long residence time in order to efficiently distribute heat to the feedstock mass usually characterized by coarse size of the components. Rotary kiln, however, is the most widespread technology applied in Municipal Solid Waste (MSW) pyrolysis thanks to the unique advantages over other types of reactors, such as the good mixing of wastes, the flexible adjustment of residence time and the large channel for the waste stream which allows feeding of heterogeneous materials, and thus, extensive pre-treatment of wastes is not required. Moreover the maintenance of the plant is quite simple. Finally, the characteristics of the kiln make the use of pyrolysis gas for heating purposes easy.

Fluidised-bed reactors are characterized by a high heating rate and good blending of the feedstock. Therefore, such reactors are more frequently used to describe the influence of temperature and residence time on pyrolysis behaviour and products. Typically, fluidised-bed reactors are used to investigate the behaviours of flash pyrolysis and to explore the secondary cracking of tar at longer residence times. Although fluidised-bed reactors have been extensively adopted in laboratory studies, their industrial application is not common for pyrolysis because of the separation of bed material from coke, along with its external heating and recirculation, is complicated. Moreover, wastes pre-treatment should be dealt with thoroughly, as they are expensive steps.

Tubular reactors include a family of reactors with fixed walls in tubular shape through which the materials move via various driving modes. Tubular reactors are generally heated from outside, exploiting different calorific sources. The advantages of these systems include continuous coke and gas removal from the reactor tubes, and larger heat transfer surface per unit volume; moreover, they appear to be convenient for syngas reforming. It is easy to design and run a tubular reactor if the heat transfer coefficient is known because of its simplicity and safety. However, tubular reactors have the same rigid requirements for waste pre-treatment as the fluidised-bed reactors due to the small channel for waste passage. In addition, erosion caused by continuous scratches from hard solids contained in the waste can be a risk for this reactor, and heat transfer coefficients are not well defined for different waste types [30].

1.7. Governing variables on pyrolysis processes

There are many variables governing the pyrolysis process, and not all of them can be easily adjusted. Some of them however have a major influence on the yields and characteristics of the pyrolysis products and can also be governed and tailored and they will therefore be discussed.

The main variable affecting waste pyrolysis is the temperature at which the process is carried out. The minimum pyrolysis temperature required for the complete degradation depends on the processed type of waste. Together with the residence time, temperature affects the percentage of degradation of the product, while with pressure, heating rate and superficial velocity of the carrier gas, plays an important role in the occurrence of secondary reactions and then both in product yields and properties. Increasing flow rate of the carrier gas or performing the process under vacuum pressure, decrease secondary reactions in gaseous phase attaining almost unchanged the product yields as the temperature increase. Otherwise, an increase in the temperature could promote an increase in the gas fraction yield at expenses of the liquid fraction yield.

It is generally assumed that in thermochemical processes small particles display an isothermal behaviour and have no hampering to internal heat transfer, hence no temperature gradients should be observe inside the material contrarily to what observed for large particles. Although it is well-known that particle size affects the pyrolysis kinetics and the internal heat transfer affecting the pyrolysis products yields and properties, there are only few studies regarding the influence of particle size on the performance of the pyrolysis process.

Reducing the size of the waste requires an energy consumption that is only partly compensated by the reduction in process times. Oyedun et al. [52] confirm that there is a trade-off between the overall energy used for shredding and the time required to complete the process: the smaller are the particle sizes the shorter is the time required for completing the pyrolysis process though the overall energy required is higher.

The heating rate affects the heat transfer phenomena influencing the pyrolysis time, and consequently the gas, liquid and solid product distributions and their physicochemical properties. Depending on the applied heating rate, pyrolysis can be classified in slow, fast and ultra-fast.

- Slow pyrolysis involves a slow pyrolytic decomposition at low temperatures. The process is characterised by low heating rates and sometimes by low temperature. In these conditions both solid and vapour stay at high temperature for longer times (in the order of minutes to hours) and this results in secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products. This behaviour makes the slow pyrolysis also be labelled as carbonisation. Unlike fast pyrolysis, the objective of the slow pyrolysis is the char production, although tar and gases are also obtained but not necessarily recovered and valorised.
- Flash pyrolysis requires a rapid thermal decomposition characterized by high heating rates. This process usually requires a feedstock with small particle sizes and devices with special design to allow quick removal of the released vapours. High heating rates with short residence times in the hot zone and rapid quenching of the products (volatiles) favour the formation of liquid products, since the volatiles released in the pyrolysis process are condensed before further reaction breaks them down to lower molecular weight species, such as gaseous products. Thus, a liquid fuel with a higher calorific value is obtained. In fact, fast pyrolysis is recognised as an effective route for the production of liquid fuels and added-value chemicals with higher yield. Fast pyrolysis is usually performed in fluidised beds, entrained, ablative and free-fall reactors where the reaction time is of the order of milliseconds to seconds. It is generally accepted that the volatiles residence time must be lower than 2 seconds. Longer residence times result in significant reductions of organic products resulting in the occurrence of secondary reactions as thermal cracking.
- Ultra-fast pyrolysis refers to thermal cracking under conditions of high temperature and reaction time much less than 500 milliseconds, heating rate greater than 1000°C/s, and rapid product quenching [29].

2. Scope

Waste generation and management are two key points among the environmental priorities of the European political agenda. This is due primarily to the massive, and still growing, amount of wastes involved and to the high impact that they have on the environment and human health. The European “Waste hierarchy” pursue, as its first objective, the reduction of the total waste generated, and as the second, the promotion of recycling and incineration with energy recovery at expense of traditional landfill. Such a system of waste management is not possible without proper garbage differentiation and application of schemes of treatment conveniently suited to maximize the production of secondary raw materials, in order to minimize the environmental impact both in process emissions and in exploitation of primary resources.

In this context, a project takes shape, which started in September 2009 by Curti Costruzioni Meccaniche SpA (Castel Bolognese, RA), in particular within its Energy Division based in Modena under the project "Ecosystem for disposal of used tires ", funded by the Emilia-Romagna and in the context of the POR-FESR 2007-2013 and PRRITT 2008. The project involves the collaboration of CIRI-MAM (Interdepartmental Center for Industrial Research on Advanced Applications in Mechanical Engineering and Materials Technology, University of Bologna), DCIM (Department of Industrial Chemistry and Materials Engineering, Faculty of Industrial Chemistry, later Department of Industrial Chemistry “Toso Montanari”, University of Bologna), DIEM (Engineering Department of Mechanical, Nuclear, Aviation and Metallurgical Engineering, Faculty of Engineering, later Department of Industrial Engineering, University of Bologna) and LEAP (Laboratory Energy & Environment Piacenza, Polytechnic University in Milano).

The objective of the project is the treatment of waste streams characterized by highly differentiated management in an innovative plant, able to guarantee a high safety of the process thanks to the presence of a hydraulic guard.

In this PhD work the whole set up and run of the innovative pyrolysis pilot plant (Figure 2.1) was addressed and the activities carried out in the facilities offered by the Faenza Tecnopolo site (Faenza, RA), where the reactor was built, regarding the design, construction and direct experimentation will be reported.

The process has been initially developed for the pyrolysis of about 30 kg of whole end-life tires in order to save the energy costs of shredding. The pilot plant has thus been used to pyrolyze new tires (NT) and end-life tires (ELTs) at temperatures from 400 to 600°C with step

of 50°C in presence of steam. The properties of pyrolysis products were characterized using different techniques and the influence of temperature, state and type of tires on product yields has been studied in order to identify key features to modulate the process.



Figure 2.1 – An image of pyrolysis pilot plant.

After optimizing the pyrolysis process in the pilot plant, the same reactor has been used, among others, to study the feasibility of a process of recovery high added value reinforcements from carbon fibers reinforced composites (CFRCs) materials. To better understand the potential and the real recycling capability of the process, up to 70kg of both uncured materials (prepregs) and cured composites, both coming from different stages of the manufacturing process, have been pyrolyzed in the 450-600°C range. The solid residue (carbon fibers covered by a carbonaceous layer) has been subjected to a further oxidative step at 500 and 600°C for different residence time to provide fibers devoid of any organic residue that did not volatilize during pyrolysis. The effects of both pyrolysis and oxidative process on the recovered fibers were evaluated and the reinforcement behavior of pyrolyzed and pyrolyzed/oxidized chopped fibers, compared to virgin fibers, was tested in the production of new Chopped Carbon Fiber Reinforced Composites.

Finally, the same process has been conducted on fiberglass/polyester composites. The products obtained upon the polyester resin decomposition have been fully characterized. The effect of the oxidative step on the recovered glass fibers, obtained in different working conditions, has been observed in order to evaluate the adaptability of the process of recovery of the fibers from this type of waste.

3. Results and discussion

All the pyrolysis processes presented in this thesis have been conducted in the Curti Costruzioni Meccaniche SpA pilot plant installed at the Faenza Tecnopolo site (Faenza, RA) [54].

3.1. Optimization of the plant

When the pyrolysis pilot plant was first built, the first effort was put forward for the definition of a solid standard test routine to be applied in the further runs. In this section the approach adopted to reach such optimized run conditions is thoroughly described, from the beginning to the full optimization of the whole system.

3.1.1. Dry run

The pilot plant was first started at the beginning of October 2011. The first tests carried out on the plant were five dry run in order to verify the actual and sound functioning of the system. The tests were used to verify:

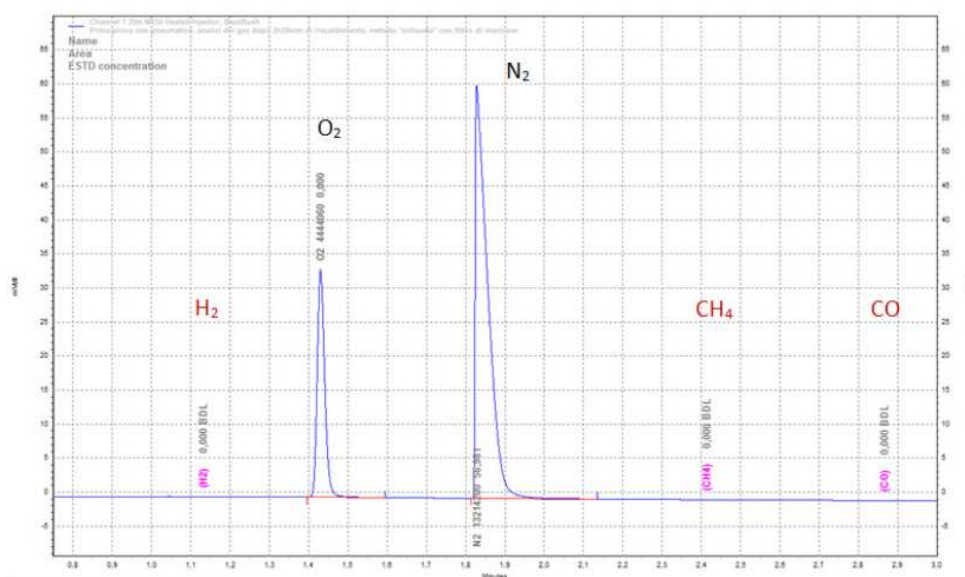
- the actual functioning of the resistance;
- the effectiveness of the insulation;
- the sealing efficiency of the reactor and other accessories;
- the sealing efficiency of flanges and taps;
- the correct working conditions of the extractor elements;
- the correct working conditions of the management software system.

These preliminary tests resulted in the identification of a very critical condition: owing to the presence of an hydraulic safety sealing for the batch, during the heating step an excessive amount of water evaporated from the pyrolyzer tank collecting in the demister. In order to reduce the volume of the evaporated water without nullifying the usefulness of the hydraulic seal, a floating cover layer hinged to the pedestal of the sample holder has been designed and installed just below the sample holding platform in the middle of the tank: the size of the floating device is slightly lower than the inner diameter of the reactor and is shaped slightly like a cone, such as a so called "Chinese hat". This device strongly reduces the water surface exposed within the pyrolysis chamber, thus hampering its evaporation, without cancelling the safety role of the hydraulic seal.

3.1.2. Run with tires

Once the preliminary criticality were identified and solved, forty-six pyrolysis tests have been carried out with tires as a feedstock with the main objective of defining a solid standard test.

The first test was carried out with 3.10kg of samples (half tire) and had a duration of 100 minutes. The characteristics of the plant, as it was at that moment, allowed to reach the maximum temperature of 369°C. Due to the small amount of loaded sample and to the low temperature achieved, this first test did not lead to the production of a quantity of gas such as to fill the volume of the system until reaching the μ -GC that, consequently has not detected syngas production but only the presence of air: O₂ and N₂ in the MS column (Figure 3.1) and CO₂ in the PPU column. In addition, at the end of the run, when the reactor bell was lift up the tank of the pyrolysis reactor, the sample appeared shortly degraded.

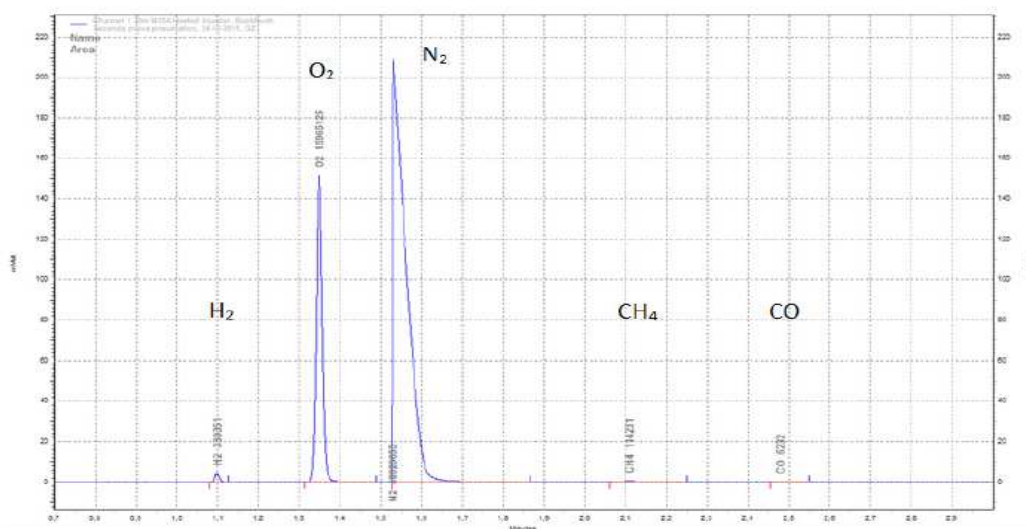


3.1 - Chromatogram of the MS column for the analysis carried out during the first test run.

The second test was carried out with a whole tire and increasing the testing time to 375 minutes (6h, 15min). Despite the long time allowed for the experiment, the maximum temperature reached was 397°C and, at the end of the run, the residue displayed a neat detachment of the tire tread from the carcass, which however maintained the original round shape thanks to the steel filaments in the inside. The thermal decomposition of part of the tire is demonstrated by the detection of traces of syngas, as reported in the chromatogram displayed in Figure 3.2, where signals ascribed to H₂ and CH₄, as well as O₂ and N₂, as observed.

The test allowed to highlight again some criticality: the first one is linked to the floating device, which during the heating of the reaction chamber partially sunk, probably owing to the weight of the condensed vapour entered into the chamber via the compensation valve. The malfunction caused the evaporation, and subsequent condensation in the demister, of a large amount of water (147,05 kg equal to 24.8 kg/h). A second issue was related to the failure in achieving the set temperature even with long test times.

With the aim of solving the emerged problems in view of the next trial, the floating “Chinese hat” was replaced with a cylindrical watertight device, and interventions on the control software restored the full efficiency of electric heaters.

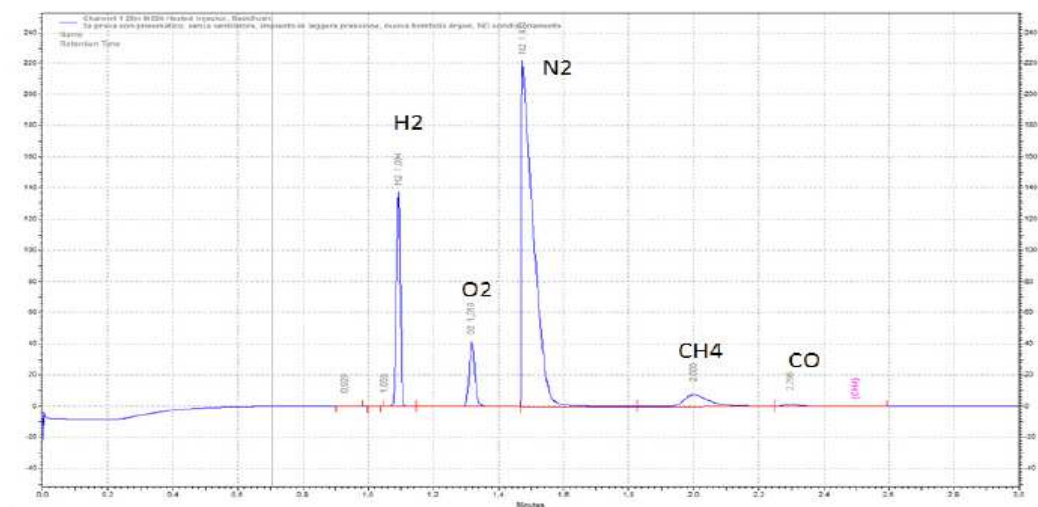


3.2 - MS column chromatogram of the evolved gases during the second test.

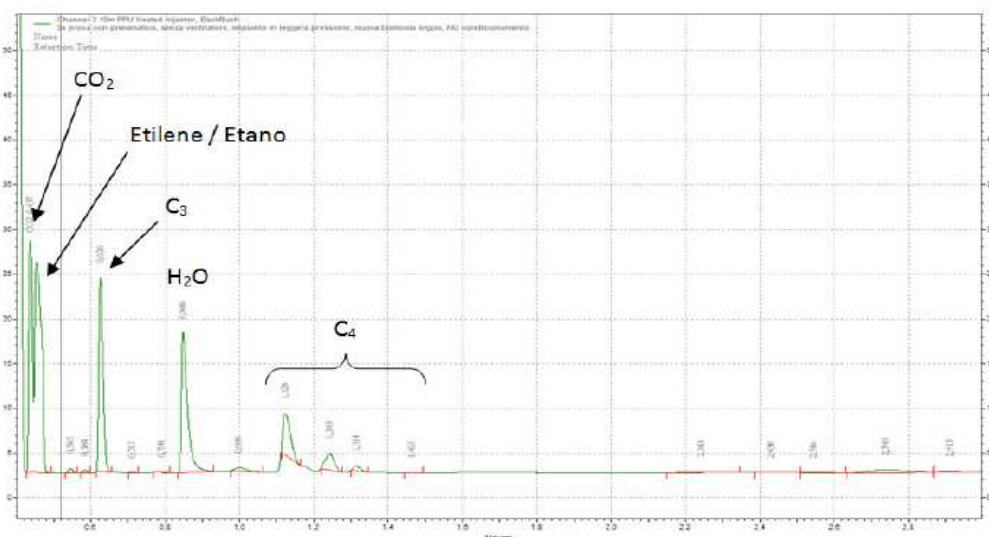
The intervention on resistors allowed, during the third test, to reach a temperature of 501°C in about 130 minutes while the improvements made to the floating device reduced the amount of evaporated water per hour (17.2 kg/h). The test lasted a total of 325 minutes (5h, 25 min) and this time the process resulted in the complete degradation of the sample. However, during the test the μ -GC continuously detected the presence of both O₂ and N₂, with a nearly air ratio. The cause of this anomaly has been attributed to some leakage along the line, possibly due to sealing problems, which have the effect of diluting the syngas product. The search for possible leaking points identified the fan as the main responsible for the problem.

The 4th test has been thus carried out excluding the fan by using a by-pass on the line. The test has been therefore carried out under pressure with a total duration of 260 minutes (4 hours, 20 min), reaching 500°C.

The absence of continuous aspiration, thanks to the fan bypass, has also led to a lower extraction of water vapours from the hydraulic seal, the hourly evaporation of H₂O being further reduced down to 11.8 kg/h. The lack of leakage improved the detection of the components of syngas by the μ -GC, since much more intense signals were observed (Figure 3.3 and Figure 3.4), confirming the responsibility of the fan in the air infiltration. Nevertheless, the air components are still present, hinting to the presence of some additional leakage still not detected.



3.3 - MS column chromatogram of the evolved gases during the 4th test.



3.4 - PPU column chromatogram of the evolved gases during the 4th test.

The 5th and 6th tests have been carried out in the absence of the extraction fan, temporary removed from the reactor, and they both aimed at studying the best thermal

gradients inside the pyrolyzer and the further reduction of the water evaporating during the process. The latter goal has been achieved by inserting an O-ring resting on the upper face of the floating device, along its outer circumference, so as to further reduce the space left to the inner wall of the reactor. The O-ring is made of a steel core welded at the ends to obtain a circle of the size of the inner wall of the reactor, covered with bandages of ceramic fabrics to obtain a thickness of about 3 centimetres. The adoption of this solution has proved particularly effective, reducing the water evaporation to 4.7 kg/h.

The 7th and 8th tests were carried out once again with the extraction fan. Moreover, a careful verification of the seals, highlighted additional leakages along various gas lines. It was also noted that the complete emptying of the demister was very challenging, hence resulting in its modification: the drain valve of the condensed products has been moved further lower and the demister tank has been tilted by a few degrees for the complete drainage of the liquid towards the tap. It was not possible to provide a greater inclination since the demister is directly connected to the cooling coil used to condense the oil phase from the volatiles via rigid pipes that would not allow further tilting other than the already installed shims placed opposite to the tap. Finally it was open an inspection window, on the side of the faucet. It is an opening of rectangular shape closed by a tempered glass and a silicone seal, kept with a frame bolted to the structure. The purpose of this modification is the visual inspection of the contents of the demister and the ability to perform a complete cleaning of the tank. After this amendment, a suction system it was also created, that was operated during the operations of opening and cleaning of the demister. A suction device was then fixed above the opening, through a flexible hose, to the intake system of the laboratory.

Subsequent 9th and 10th tests allowed to check the efficiency of the extraction fan. The data recorded by μ -GC showed that there is still the problem of air infiltration. In fact, the concentrations of N₂ and O₂ detected by the instrument are about 78% mol/mol of N₂ and 21% mol/mol of O₂, while the compounds of the syngas are detected in concentrations too low to be appreciable. The strong effect of dilution caused by the introduction of air also creates problems for the syngas combustion. In fact, being too diluted, the combustible gas fails to ignite sustain the flames of Bunsen burners. The presence of pilot flames, powered by LPG and placed above each beak, nevertheless ensures the full combustion of the gases produced before reaching the outer chimney.

The 11th test was planned to verify that the gas produced by the process was in fact a fuel gas and especially to identify the range of production of syngas. To help achieve this objective 3 tires have been loaded (16.59 kg) in order to increase the amount of products and

the fan was again excluded to avoid air infiltration, thus operating in overpressure. The pilot lights were periodically turned off in order to attempt ignition of the produced gas from the reactor. After 100 minutes from the beginning of the run the syngas finally burned (Figure 3.5). This result well compares with the expected timing as evaluated by preliminary TGA results of these tires, by the control of the temperatures and by experimental measurements of the values of the internal pressure of the reactor, measured by the pressure in the head to the bell.



3.5 – An image of the first ignition of the syngas produced by pyrolysis of tires in the pilot plant.

In this test a delay of 15 minutes between the change in pressure in the reactor and the arrival of the combusting gas to the end-of-line torches was observed. This is due to the filling time of the line in the plant, the time increasing in the tests where the fan is off.

The tests from 12th to 15th have been carried out under a slight vacuum, maintaining a relative pressure in the reactor of -7 mbar. It was also decided to avoid pre-washing of the reactor and of the line with N₂ flush. The reason for these choices lays on the assumption that the suction and the volumes of steam produced in the heating phase of the reactor might be able to strongly reduce the presence of O₂ inside the reaction chamber. The small amount of air which remains inside the reactor could then react in the early stages of the process, leading to a gasification process. However, this gasification stage would be very short because the O₂ would be consumed in a short time, and possibly before reaching temperatures high enough to promote significantly this process.

The four tests, carried out with the same parameters, had also the objective of verifying the repeatability of the process and the consistency of the obtained results. In these tests, the gas analysis has still displayed a large amount of air and therefore an excessive dilution of the

synthesis gas, whose concentration is less than 1% mol/mol. However, the compositional trend of the obtained syngas in the repeating tests has been similar.

The 16th-18th tests, carried out by connecting the line of μ -GC upstream of the scrubber, aimed at evaluating the effectiveness of the filter through the comparison of the concentration of H₂S between these results and those from previous tests.

This solution has not proved useful for this purpose due to the high H₂S concentration, which is even above the instrument tolerable levels. However, the results strongly prove the efficiency of the filter against H₂S.

In the 19th and 20th tests, conducted at relative pressure of -3.5 mbar, anomalies in pressure detection has been observed between the reactor and the first check point along the syngas line, upstream of the cooling coil. The cause of this phenomenon has been ascribed to the presence of tarry deposits condensed in the "U" connecting pipe positioned between the reactor and the cooling coil. The insulation of the pipe was insufficient to prevent the condensation of substances with high boiling point, and their continuous incremental deposit at the lowest point of the pipe has caused a progressive reduction of its diameter. For this reason the plant has been stopped for some manual cleaning operation, which was particularly complex due to the length of the tube and the tenacity of the tarry residue, which solidifies upon cooling. The solution to the problem has been identified in the replacement of the flexible U shaped pipe with a straight pipe, with a slight inclination towards the cooling coil for the drainage of any condensed substances. In order to facilitate future washes, this tube section was equipped with a nozzle with a sealing stopper, and a second nozzle was inserted into the tub of the demister. Moreover, all types of insulation has been removed from the connecting tube, preferring the condensation of tars in this section of pipe, easily removable and cleanable, rather than in the cooling coil where it would cause more serious problems.

Simultaneously, evidence was given of solubility of tars in various solvents and also in the very same pyrolysis oil produced from the pilot plant, which proved a good solvent for these substances.

With the first 19 tests, a good process stability has been reached, hence the research progressed, in the 20th and 21th tests, for the evaluation of the products distribution as a function of process pressure. The data demonstrates that the degradation extent is practically independent from the applied pressure.

The tests from 23th to 26th have shown a sealing problem, located on the scrubber: the exterior carpentry of the filter was old and already in use for several years on other systems designed from the company. In a test carried out under pressure, to evaluate the flammability

of the syngas, a leakage of gas from the bottom of the structure that encloses the filter elements has been noticed. The paint which covers the structure has probably hidden this corrosion problems. It has therefore been necessary a total reconstruction of the external structure using stainless steel, which more resistant to corrosion (Figure 3.6). In the same context the filter material has been renewed.



3.6 – Steel carpentry of the new filter.

The tests from 27th to 36th have been performed in absence of the acid gases scrubber along the line which had forced to perform the tests with a constant control of the H₂S concentration in order to switch off the μ -GC in the presence of concentrations above 1.3 % mol/mol.

The 27th test had the purpose of evaluating the time required for the complete combustion of all the produced syngas. To induce the escape of the produced gas from the bell, the resistances were kept activated until the extinction of the flames at the burners. This procedure allows a continuous production of steam which drives the syngas along the line. The total duration of the test was 310 minutes (5 hours, 10 minutes).

The 28th and 29th tests were conducted with the aim of verifying the possibility of reducing the test time without compromising the complete degradation of the sample. These tests lasted 80 and 90 minutes respectively. Any detected variability in product yields can be ascribed to the difference in the duration of the test.

The tests from 30th to 32th have been carried out in the absence of scrubber and with the fan switched off in order to stabilize the syngas flow, favouring its complete combustion.

The tests from 33th to 37th have been conducted with the aim to define a standard procedure and the optimized plant system structure. At the end of these tests the new filter for the abatement of acid gases has been installed. Its presence allows to monitor the composition of the produced syngas, for the entire duration of the test.

The tests from 38th to 42th have been interrupted due to electricity interruption caused by adverse weather conditions. The data obtained in these tests were then used to evaluate the effect of incomplete degradation in the process of pyrolysis of tires.

The tests from 43th to 46th coincide with the insertion of some substantial changes in the system:

- 8 additional resistors have been installed in the double wall of the reactor to reach a total power of 2100W. These resistors can be independently activated with respect to the first installed resistors. With this arrangement it is possible to increase the thermal gradient from 5°C/min to 8°C/min thus reducing the time required to reach the set-point temperature.
- The fan has been replaced in order to avoid air infiltration with a different sealing system, more suitable to the needs of the experiment. Thanks to the new fan the air infiltration have been eliminated, and the analysis of the syngas composition are finally truly significant.
- The demister has been further modified: the entire bottom plate of the tank has been replaced, and is now designed with an inverted pyramid shape bottom, with a tap at the lower top of this pyramid for easily emptying the liquid products. Following this, the window for internal inspection has been considered no longer necessary and was then sealed. The welding of all these new parts required a series of leakage tests to verify the presence of welds defects, with consequent air infiltration and loss of gas and/or liquid.
- The first installed burners were replaced with the new ones, more suitable for the gas produced.
- The first installed fume hood, where the end-of-line burners are placed, has been entirely rebuilt. The new hood has been designed to withstand the high temperatures possibly developed with the new combustion system.
- On top of the hood a fan was placed that ensures the aspiration of the combustion fumes and their transfer to the chimney, while a ceramic filter element for reducing pollutants in combustion has been placed in front of the fan.

The subsequent tests have been the subject of the research activity aimed to recovery secondary raw materials from tires, Carbon Fibers Reinforced Compounds (CFRCs) and Glass Fibers Reinforced Compounds (GFRCs, or fiberglass).

3.1.3. Standard tests

The research activity led to the submission and publication of peer-review papers, thus, according with the copyright of each editor, the description will be disclosed using part of the manuscripts (text, figures and tables). No significant change will be applied to the already published materials, with the exception of some integration of data obtained after the submission/publication or stylistic adjustment in line with the format of the work.

3.2. TiresThe pyrolysis on new (NT) and end-life (ELTs) tires has been conducted on the whole objects in order to recover energy and materials and simultaneously save the energy costs of their shredding.

The different tires wear status implies the variation, from set to set, of the degradable/non-degradable components weight ratio. For this reason, the average composition weight percent of steel for each main set of tests, compared to the average total weight of the treated material, is reported in Table 3.1.

Table 3.1 - Average composition (wt%) of steel in the principal significant sets of the investigated tires.

Process temperature (°C)	State of tires	Composition (wt%)	
		Steel	Other
400	NT	9.2	90.8
450		9.1	90.9
500		9.1	90.9
550		9.0	91.0
600		10.0	90.0
400		ELTs	12.5
450	13.0		87.0
500	12.5		87.5
550	12.4		87.6
600	11.6		88.4

3.2.1. Preliminary thermogravimetric investigations

In order to investigate the thermal behaviour in pyrolysis conditions, a Atracta-Lassa 155/70R13 79T has been used to perform thermogravimetric analysis (TGA) in inert atmosphere (N_2). The thermograms obtained at heating rates of 5 and $10^\circ\text{C}/\text{min}$ and a maximum pyrolysis temperatures of 400, 500 and 600°C for the representative sample of automotive tire waste are presented in Figure 3.7.

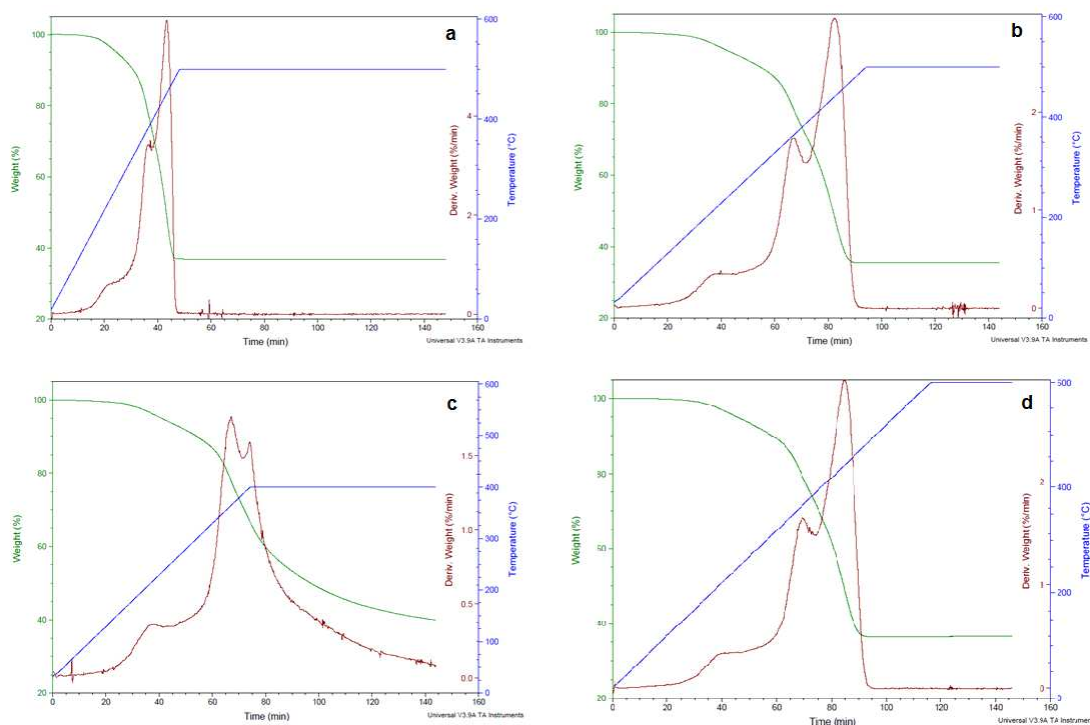


Figure 3.7 - TGA thermograms for automotive tire wastes. a: heating rates $10^\circ\text{C}/\text{min}$, $T_{\text{max}} 500^\circ\text{C}$; b: heating rates $5^\circ\text{C}/\text{min}$, $T_{\text{max}} 500^\circ\text{C}$; c: heating rates $5^\circ\text{C}/\text{min}$, $T_{\text{max}} 400^\circ\text{C}$; d: heating rates $5^\circ\text{C}/\text{min}$, $T_{\text{max}} 600^\circ\text{C}$.

When keeping the maximum reached temperature unchanged (500°C , Figure 3.7, a and b), it is possible to observe the thermal gradient effect on the degradation rate, that increases as the heating rate is increased. Consequently, the duration of the thermal decomposition is shorter for the higher thermal gradient (17 minutes at $10^\circ\text{C}/\text{min}$ against 35 minutes at $5^\circ\text{C}/\text{min}$). On the other hand, the heating rate has no influence on the range of temperatures in which the decomposition takes place which is located between 350 and 425°C with a maximum speed of decomposition at 425°C . In both cases, the increase of temperature between 450 and 500°C does not involve further loss of weight of the samples whose residue stabilizes at around 35%.

At constant heating rate (5°C/min, Figure 3.7 b, c and d), the maximum reached temperature affects the completeness of the process. At 400°C (Figure 3.7 c), the main thermal event is interrupted when the set point temperature is reached with consequent incompleteness of the process and a high solid residue (about 40%). At 500 and 600°C (Figure 3.7 b and d) the obtained thermograms are completely similar so, above 500°C, no further modification of the sample occurs.

In all thermograms three peaks are clearly observed in the first derivative curve of the weight loss. The weight loss that occurs before 200°C is probably due to the evaporation of moisture [55]. Subsequent weight losses are divided into two distinct thermal events (about 370 and 425°C), more resolute for low heating rates. These can be attributed to the different temperatures of pyrolysis of the major rubber components of the tires. In particular, the natural rubber (or synthetic polyisoprene derivatives) decompose at lower temperature (about 375°C) with respect to the styrene-butadiene rubber [56, 57].

3.2.2. Pyrolysis yields

The aim of this research is to study the influence of the maximum reached temperature and of the state of wear on pyrolysis products in presence of steam, the develops due to the peculiar characteristics of the reaction chamber. Being the steel content in each set of tires variable (see Table 3.1), the products yields (Figure 3.8) are net of steel. The obtained trends reported in Figure 3.8 are similar for both tire series in the studied temperature range. It is worth noting that the highest carbonaceous residue (char) has been achieved in tests carried out at 400°C for both NT (49.6 wt%) and ELT (49.5 wt%). Such a behaviour suggests that at this pyrolysis temperature, even for protracted times, it is not possible to achieve a complete thermal degradation of the polymeric fraction. Furthermore, the composition of the pyrolyzed gaseous fraction is rich in light compounds (syngas) due to the cracking of the long molecular chain (oil) and it is favoured at long residence time. In other words, at 400°C, the low amount of degraded rubber and the low thermal expansion inhibit the gas exit from the reaction chamber with consequent longer residence time which involves additional molecular cracking of the oil fraction [58]. Between 450 and 600°C, the thermal degradation of tires increases, as demonstrated by the decreasing of the char portion which reaches a constant value around 40 wt%. At these temperatures, the produced gaseous fraction tends to spontaneously flow out the reaction dome, favoured also by the increase of the thermal expansion of the gases, thus cooling down and interrupting the subsequent cracking reactions. This effect results in an important increase of the oil fraction between 400 and 450°C for both series (from 14.0 to 29.9

wt% for NT and from 12.1 to 26.0 wt% for ELTs) and a slight decrease of the incondensable fraction. Between 450 and 600°C, a further slight enhancement of the oil fraction with a corresponding decreasing of syngas takes place. It is important to note that for both sets of experiments, between 500 and 550°C, the oil/syngas weight ratio reaches the value of 1.

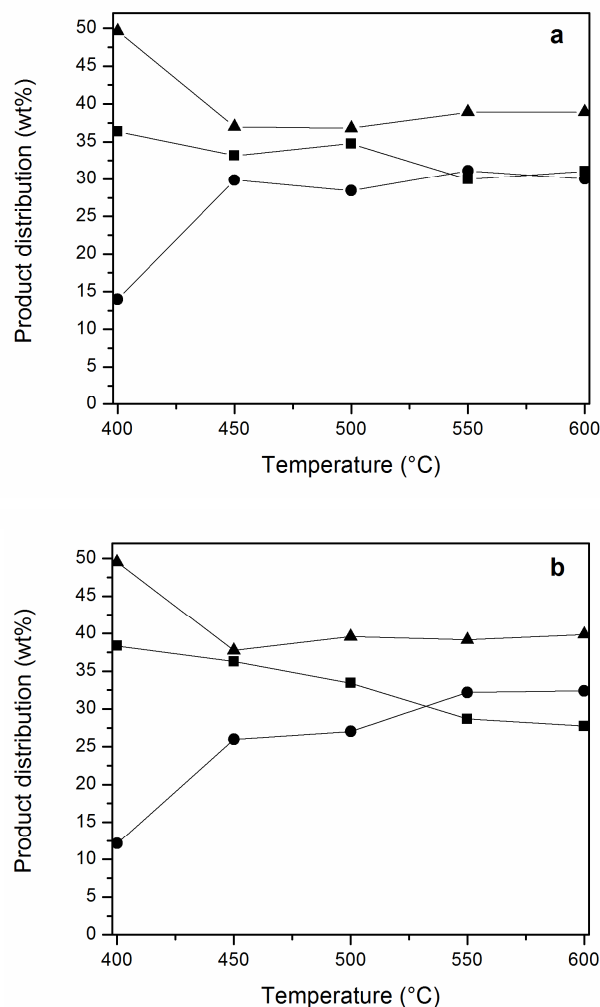


Figure 3.8 - Effect of temperature on the yield of the different pyrolysis products. (a) NT and (b) ELTs: (▲) Solid residue; (■) Syngas; (●) Oil.

Many scientific investigations on pyrolysis of grinded tires are reported in the literature. In Table 3.2 have been collected the results of some of them, thus showing how different technologies (i.e. type of reactor) and process parameters (i.e. temperature, pressure, heating rate, residence time) can lead to very different products yields. The oil fraction, for example, covers an extremely wide range of fractions and its trend with the increase in temperature is not constant. In the tests carried out with experimental condition similar to those presently

reported, the oil yield has a stable/slow increasing trend with the increase in temperature [8-10, 46, 37, 59]. In these tests, the yield in syngas, also at low temperatures, is noticeably higher than what reported by other authors (Table 3.2). In particular, pyrolyzing non-shredded tires at 500°C, Roy et al. [42] obtained a smaller amount of incondensable gas and a bigger oil fraction. Furthermore, according to Kaminsky and Mennerich [59] that evaluated the effects of the presence of steam on the pyrolysis process of tires at 500°C in a fluidized bed reactor, the yield of pyrolysis products results not significantly influenced by this process parameter.

Table 3.2 - Literature survey of results of the waste tires pyrolysis.

Experimental system	Ref.	Process (°C)	Note	Yields (wt%)		
				Char	Oil	Syngas
Autoclave	[8]	300-700	feedstock size $\approx 3\text{cm}^2$; heating rate $15^\circ\text{C}/\text{min}$	88-44	5-38	7-18
	[9]	400-700	Radial portion (175g) heating rate $15^\circ\text{C}/\text{min}$	53-43	28-40	7-9
Horizontal oven		400-900	feedstock size $< 2\text{cm}$	68-38	31-57	1-5
	[10]	500	heating rate $10^\circ\text{C}/\text{min}$	47	42	11
		550-800	heating rate $7^\circ\text{C}/\text{min}$	34-33	56-55	8-9
Conical spouted bed reactor	[39]	425-600	feedstock size $< 1\text{mm}$	34-36	64-56	2-8
Static-bed batch reactor	[11]	450-600	feedstock size 4.5cm^3 , including metallic and textile part	37-38	58-53	4-9
	[59]	400-700	feedstock size 2cm, including metallic and textile part	64-51	30-43	2-4
Fluidized bed reactor	[46]	360-810	feedstock size 0.32mm	40-30	50-30	10-40
		500-600	feedstock size 1-2mm	30-40	65-51	5-9
	[60]	500	feedstock size 1-2mm presence of steam	31	65	3.5
Pyrocycling process	[42]	500	under vacuum (7 kPa), whole tires, 10% steel	37	47	5
Rotary kiln	[61]	550-680	feedstock size $< 2\text{cm}$	49-49	38-32	2-11
Fixed bed reactor	[47]	400-700	shredder sample	62-41	31-40	7-19
	[62]	375-575	motorcycle tires, feedstock size 4cm^3	50-40	42-42	8-18

3.2.3. Oil characterization

In order to evaluate the influence of the different process parameters, the oils obtained from different pyrolysis tests have been analyzed in terms of both fuel characteristics and chemical composition.

Elemental composition of the presently investigated samples is similar to that of previously reported pyrolytic oils (Table 3.3). However, the determined sulphur content (about 1.0-1.1 wt%) is lower than that reported in the literature and it is interestingly around the threshold for the potential marketing of this product as a low sulphur containing fuel. From these data it is possible to calculate, through the ASTM D 1552-07, the relative calorific values (around 10300 kcal/kg) which, as expected, are similar or slightly higher than what reported in the literature for similar processes.

Table 3.3 - CHN-O/S analysis and calorific values for the investigated oils compared with literature data.

Sample	Process (°C)	Elemental composition (wt%)					GCV (kcal/kg)	NCV (kcal/kg)
		C	H	N	O	S		
NT	400	86.0	11.1	0.6	1.2	1.1	10300	9700
	450	85.9	11.2	0.5	1.4	1.0	10300	9700
	500	85.8	11.3	0.6	1.3	1.0	10300	9700
	550	85.7	11.3	0.6	1.4	1.0	10300	9700
	600	85.7	11.5	0.5	1.3	1.0	10400	9800
ELTs	500	85.9	11.2	0.5	1.3	1.1	10300	9700
[8]	500	85.6	10.1	0.4	-	1.4	10055	-
[11]	500	84.9	10.2	0.5	3.1	1.3	10071	-
[63]	450	78.2	10.0	0.4	-	1.4	9268	8696
[64]	650	87.57	10.35	<1	-	1.35	9952	-

The influence of the pyrolysis temperature on the oil density and dynamic viscosity is reported in Figure 3.9. The densities values tend to a slightly increase with increasing pyrolysis temperature and are quite narrowly distributed (0.93-0.97 kg/m³), in line with the value (0.95 kg/m³) reported in the literature [39, 42] and higher than those measured on a commercial diesel (Eni- Blue diesel+, 0.84 kg/m³). The dynamic viscosity of the oils tends to decrease rapidly between 400 and 550°C (from 36.73 to 18.20 cPs) where it marks its minimum. The values of viscosities of oils produced between 500 and 600°C are similar to those recorded for commercial diesel fuel.

In order to evaluate the possible effects of the aging of the oils, the samples have been analyzed immediately after the process and after further 6 and 12 months (Figure 3.2). The density and the viscosity of the oils do not show substantial variations with aging and with the wear status of the tires. These results are in good agreement with previous reports [62].

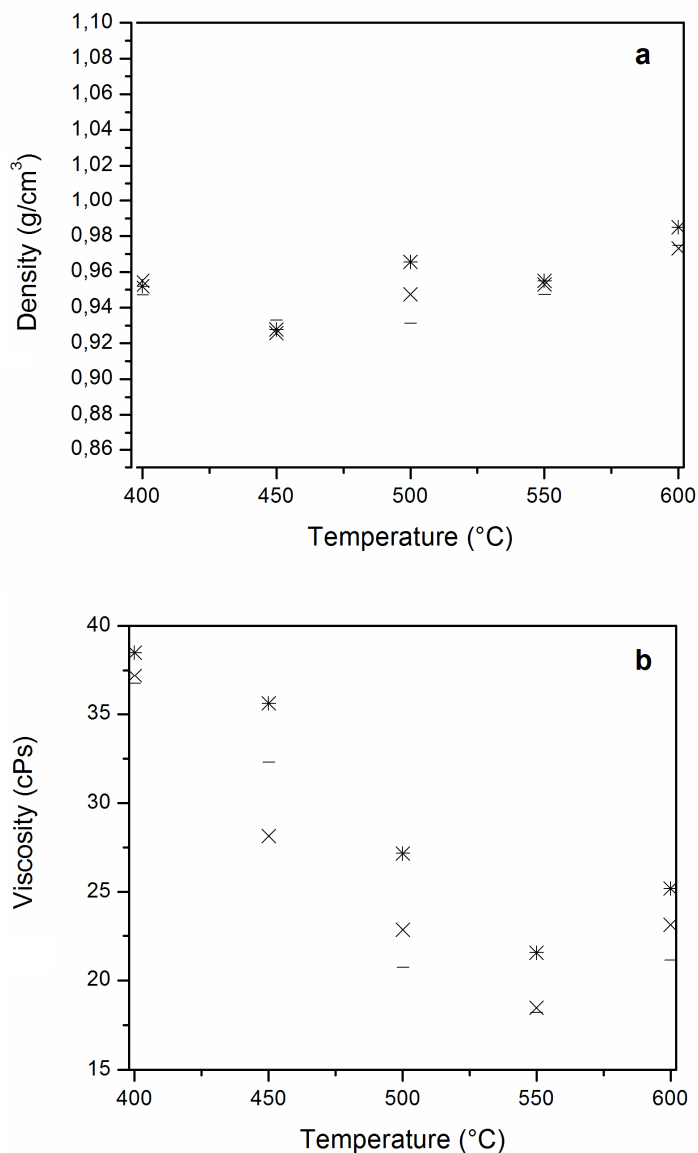


Figure 3.9 – (a) Density and (b) dynamic viscosity at 25°C of investigated pyrolysis oils at three different aging times: immediately after the process (-), at 6 (+) and 12 (*) months.

GC-MS allows to identify and quantify the chemical composition of the lighter fractions of the oil. Significant amount of benzene, toluene, ethylbenzene, xylene and styrene derived by Styrene-Butadiene rubber component are produced (Table 3.4).

Results and discussion

Table 3.4 - Yields (wt% on total oil) of the identified major compounds in C₅-C₁₂ fraction oil.

Process temperature (°C)	NT					ELTs
	400	450	500	550	600	500
TOT C₅	0.05	0.05	0.02	0.03	0.02	0.04
Aliphatic acyclic hydrocarbons	0.05	0.04	0.02	0.02	0.02	0.03
3-methylthiophene	0.00	0.01	0.00	0.01	0.00	0.01
TOT C₆	0.04	0.24	2.16	1.98	2.16	1.00
Benzene	0.02	0.23	2.15	1.97	2.15	0.99
Phenol	0.02	0.01	0.01	0.01	0.01	0.01
TOT C₇	0.37	2.69	9.30	9.79	9.98	7.23
Substituted cyclopentenes	0.00	0.02	0.01	0.01	0.01	0.02
Benzothiazole	0.02	0.02	0.01	0.01	0.01	0.02
methyl phenols	0.03	0.02	0.01	0.01	0.01	0.01
Toluene	0.32	2.63	9.27	9.76	9.95	7.18
TOT C₈	1.49	5.28	11.15	11.93	12.19	10.26
Ethylbenzene	0.56	2.06	2.70	3.67	3.00	2.70
p-xylene	0.72	2.56	6.67	6.50	7.20	6.33
Styrene	0.21	0.66	1.78	1.76	1.99	1.23
TOT C₉	0.22	0.21	0.21	0.22	0.21	0.21
Indene	0.01	0.00	0.03	0.02	0.03	0.01
methylstyrenes	0.04	0.04	0.02	0.03	0.02	0.03
Substituted benzenes	0.17	0.17	0.16	0.17	0.16	0.17
TOT C₁₀	0.35	0.32	0.26	0.22	0.24	0.33
1,4-Dihydronaphthalene	0.02	0.01	0.04	0.03	0.03	0.02
D,L- Limonene	0.03	0.06	0.02	0.02	0.02	0.04
Naphtalene	0.03	0.01	0.05	0.03	0.06	0.01
Substituted benzenes	0.27	0.24	0.15	0.14	0.13	0.26
TOT C₁₁	0.11	0.05	0.08	0.09	0.09	0.08
methyl dihydronaphtalenes	0.02	0.01	0.02	0.02	0.02	0.02
methyl naphtalenes	0.05	0.02	0.04	0.04	0.05	0.03
Substituted indenenes	0.04	0.02	0.02	0.03	0.02	0.03
TOT C₁₂	0.05	0.01	0.05	0.04	0.05	0.03
Substituted benzenes	0.05	0.01	0.05	0.04	0.05	0.03
C_{>12} Others	0.03	0.09	0.01	0.01	0.01	0.01
C_{≤12} NOT ATTRIBUTED	0.36	0.37	0.14	0.17	0.19	0.24
TOTAL DETECTED	2.68	8.85	23.23	24.30	24.94	19.18

These species, due to thermal decomposition of styrenic rubbers and to cyclization of olefin structures followed by dehydrogenation and Diels Alder reactions, tend to increase with the temperature process, as reported by other authors [11, 39]. High concentration of these compounds suggests a potential recovery of high value products as chemicals: xylenes can be employed in the plastics industries; toluene in the production of pesticides, dyestuffs, surfactants and solvents; styrene is one of the most utilized building blocks in the production of polymeric materials. The increase in temperature causes the formation of lower molecular weight species. The sum of the identified $C_{\leq 12}$ fractions shows a considerable increase with temperature: at 400°C, only 3% of the oil is composed of light fraction while at 600°C this value rises up to 25%. Moreover, the analysis of the C_{5-12} components shows that this is mainly made up of lighter compounds ($C_{<9}$). This trend can be attributed to the increase of thermal cracking due to the increasing temperature [11, 39]. For comparison, the same analysis has been carried out on the oil produced at 500°C by ELTs pyrolysis. The obtained data highlight that there are no significant differences with the NT 500 sample. Furthermore, the oil composition confirms the similarity found between the oil fractions for both density and viscosity and the limited aging changes, as confirmed by GC-MS analysis repeated on the same samples after 12 months.

In order to better understand the possible destinations for the pyrolysis oils, a simulated distillation using thermogravimetric method (SimDis TGA) in inert atmosphere has been performed. The results obtained are shown in Table 3.5 and Figure 3.10.

Table 3.5 - Distillation temperatures of investigated oils and other reported pyrolysis oils.

	NT					ELTs	[47]	[61]	[8]
Process (°C)	400	450	500	550	600	500	Diesel Fuel	500	500
Distilled (wt%)	Distillation temperature (°C)								
10	109.1	81.0	62.5	60.5	67.22	65.6	175	150	114.5
20	141.3	110.2	87.5	83.3	93.3	91.4	185	177	168.8
30	166.0	135.7	110.8	104.9	116.7	114.8	195	185	198.2
40	189.1	159.4	133.9	126.9	138.9	137.8	-	-	249.3
50	211.8	182.6	156.6	148.9	160.8	160.3	214	234	296.1
60	234.0	206.4	181.1	171.5	184.9	184.7	-	-	333.8
70	257.1	230.7	210.0	196.3	212.3	211.8	250	293	359.8
80	283.2	257.0	244.9	224.1	245.6	240.8	-	-	373.9
90	319.0	288.4	303.9	265.4	306.7	276.4	310	359	386.4
95	371.4	310.6	392.2	312.6	405.9	309.6	334	402	388.7

As reported in Figure 3.10, the trend of the obtained curves is almost linear until the distilled masses reach 85–90 wt%.

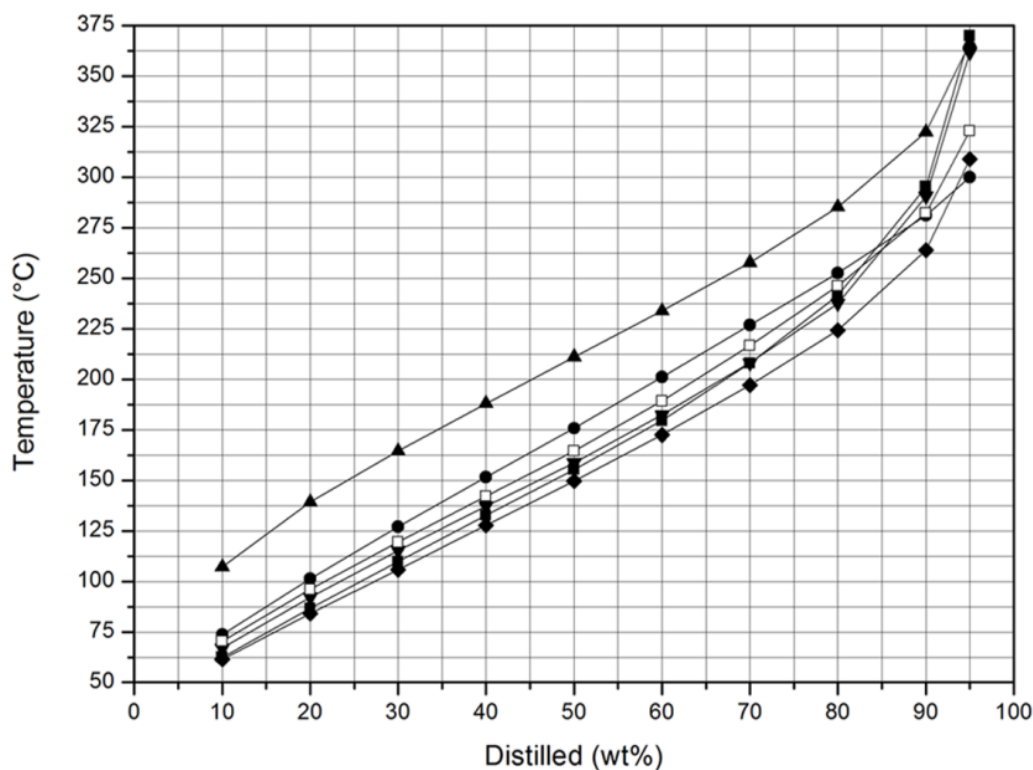


Figure 3.10 - Simulated distillation curves of pyrolytic oils obtained by means of SimDis TGA: (▲) NT, 400°C; (●) NT, 450°C; (■) NT, 500°C; (◆) NT, 550°C; (▼) NT, 600°C; (◻) ELTs, 500°C.

It is worth noting that oils produced at lower pyrolysis temperatures (400 and 450°C) are characterized by higher distillation temperature and dynamic viscosity, due to the greater content of heavier molecules. The increase of the pyrolysis temperature, instead, leads to a progressive lowering of distillation temperatures and viscosities, owing to the presence of lighter compounds. This fact is also detectable observing the distillate masses in typical temperature ranges for commercial petrol and diesel [8], as reported in Table 3.6.

Table 3.6 - Distillate mass of investigated pyrolytic oils in the typical temperature ranges for diesel and petrol.

Pyrolysis temperature (°C)	NT					ELTs
	400	450	500	550	600	500
Temperature range (°C)	Distillate (wt%)					
70-210 (petrol)	46,6	54,1	57,2	61,1	58,3	57,8
150-370 (diesel)	71,7	62,8	47,2	46,6	49,0	52,0

The amount of distillate in the lowest temperature range (petrol, 70–210°C) increases with pyrolysis temperature process whereas for the highest temperature range (diesel, 150–370°C) the trend is opposite. These data demonstrates that the composition of the pyrolysis oils, in terms of distillable fractions, is intermediate between the composition of petrol and diesel, as also reported by Ucar et al. [64].

The pyrolysis oil produced at 500°C from ETLs results richer in light compounds and more similar to petrol than other reported oils obtained in similar conditions (Table 3.5).

3.2.4. Syngas characterization

The gas mixture produced by pyrolysis of both NT and ELTs samples has been analyzed online on the plant, in order to correlate the volatile composition with the applied pyrolysis conditions.

A typical trend recordable during one run is shown in Figure 3.11.

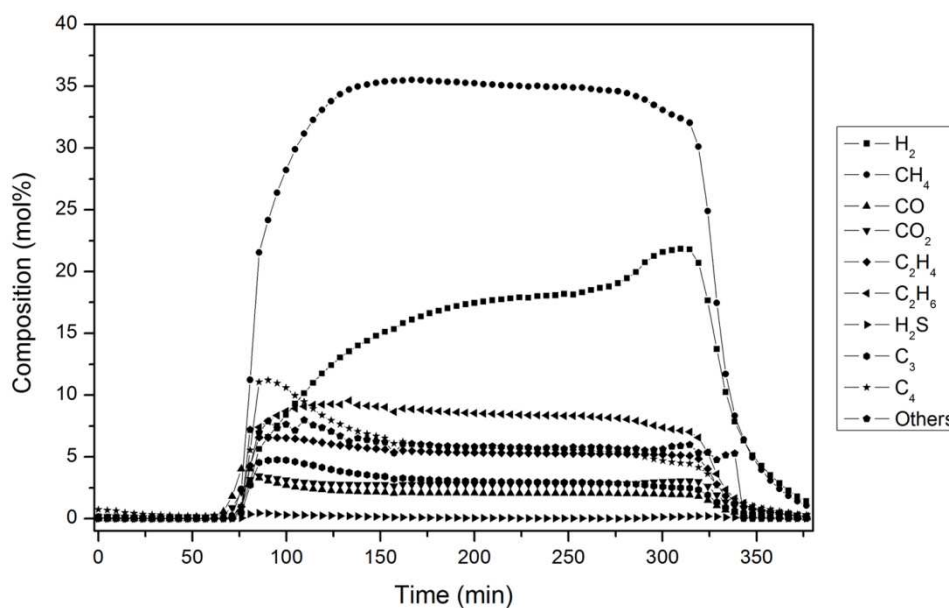


Figure 3.11 - Composition of the syngas during one run at 600°C with NT.

The average compositions of the syngas produced during the different pyrolytic experiments are reported in Table 3.7 and Figure 3.4. The measured gases are H₂, CH₄, CO, CO₂, ethylene, ethane and H₂S. C₃ is the sum of propane and propylene while C₄ is the sum of 1-butene, n-butane, 1,3-butadiene and iso-butylene. The sum of other indeterminate incondensable species is named “Others”.

Table 3.7 - Chemical composition (mol%) and GCV (MJ/Nm³) of the pyrolysis syngas produced at different process temperature.

Syngas Components	NT					ELTs				
	Process Temperature (°C)					Process Temperature (°C)				
	400	450	500	550	600	400	450	500	550	600
H₂	8.0	9.1	11.6	17.3	19.6	5.3	7.8	13.5	16.7	23.5
CH₄	20.3	21.8	27.5	32.1	39.6	17.0	17.1	27.2	31.4	34.3
CO	4.5	2.7	3.1	2.0	2.1	3.4	4.5	3.3	2.8	1.9
CO₂	5.8	5.2	4.6	3.1	2.8	6.0	7.6	5.3	4.0	3.5
C₂H₄	9.2	9.9	9.1	8.2	6.6	11.6	6.7	8.4	8.0	7.7
C₂H₆	6.6	8.6	10.6	10.0	9.9	5.9	6.1	10.1	10.0	8.7
H₂S	0.9	1.3	1.0	1.0	0.2	0.3	0.3	0.2	0.5	0.5
C₃	6.5	6.3	5.7	6.4	3.9	7.3	4.7	6.9	6.3	5.1
C₄	31.8	27.2	19.0	14.1	7.8	39.2	31.9	21.9	13.9	9.6
Others	6.4	7.9	7.8	5.8	7.5	4.0	13.3	3.2	6.4	5.2
GCV (MJ/Nm³)	62.5	61.9	57.0	52.6	47.9	67.0	63.9	55.7	52.4	46.9
GCV (MJ/kg)	45.3	46.1	46.5	48.2	49.1	45.7	44.7	46.2	47.4	48.6

It is worth noting that syngases produced by pyrolysis of NT or ELTs at the same temperature are composed of comparable amounts of gaseous species. By increasing the batch temperature, a decrease in concentration of heavier molecular weight compounds (C₃ and C₄) and a simultaneous increase of lighter species, in particular methane and hydrogen, are observed. The main compound, at process temperature $\leq 450^\circ\text{C}$, for both series, is the sum of the C₄ (between 27.2 and 39.2 mol%). Starting from 500°C the formation of hydrogen and methane increases, and at 600°C, the latter reaches almost 40 mol%. This trend, observed for both NT and ELT and reported also by other authors [8, 59], can be related to further cracking of evolved volatile matter at elevated temperatures. Contemporary a reduction in CO₂ and CO content is registered (Figure 3.12).

Kaminsky and Mennerich [60], reported that the use of steam as fluidizing medium at 500°C did not significantly affect neither yield nor the compositions of the reaction products. However, they reported that when the experiment is carried out in the presence of steam, there are high yields of CO₂ and CO which increase with the process temperatures, and lower yields of C₃ and C₄ compounds. Such a behaviour has been attributed to the reaction with water.

In our case, the amount of carbon oxides decreases with the temperature, showing that in this experimental pilot batch pyrolyzer, the presence of steam at low temperature $\leq 600^\circ\text{C}$

did not affect the composition of syngas. Thus the trend of production of H_2 , CH_4 and hydrocarbons C_3 - C_4 can be justified only by the thermal cracking reactions.

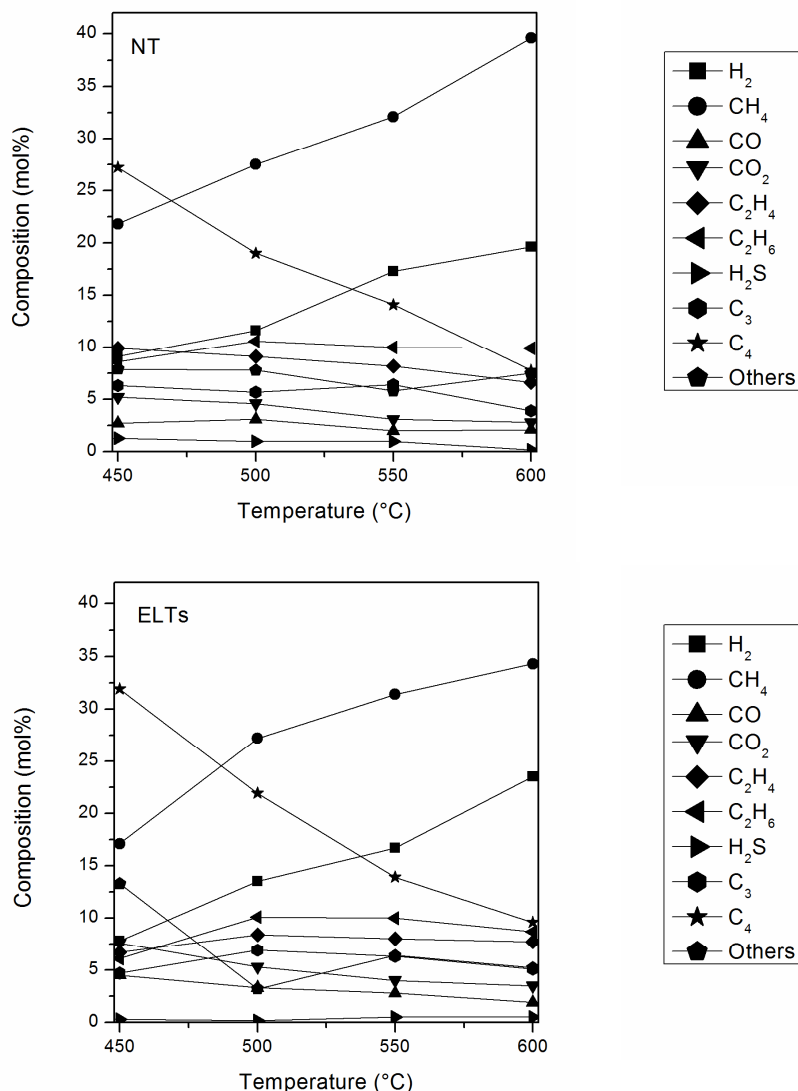


Figure 3.12 - Trend of the chemical species of the syngas as a function of temperature: (a) NT and (b) ELTs.

Finally, as reported in Table 3.7, the GCV values calculated according to UNI 7839, in the range 47-67 MJ/m^3 , decreases with process temperature for both the series. This trend is mainly due to the reduction of C_3 and C_4 molar fractions in the pyrolysis gas mixture caused by the increase of the process temperature. In agreement with the very similar compositions of syngas obtained at the same temperature, even the calorific values of the two series are almost coincident. These values are intermediate between those previously reported: 75.3-84 MJ/m^3 [8] and 47.7-39.6 MJ/m^3 [63].

3.2.5. Char characterization

The solid residue is the product most sensitive to the compositional variability of the processed tires, because in the char are concentrated, among others, sulfur and metals introduced as fillers and adjuvants in the process of vulcanization. The proximate and elemental analysis, conducted on char samples produced by pyrolysis at 500°C compared to previously reported data of char obtained in similar conditions, are reported in Table 3.8. Proximate analysis shows no significant differences between the char obtained by ELTs and NT at the same temperature.

The values obtained for moisture and ashes are in line with the values reported by other authors. The content of volatile compounds, which in literature covers a wider range, is similar to that reported by Diez et al. [63].

Table 3.8 - Proximate average and elemental analysis of char produced at 500°C for NT and ETLs compared with literature data.

Sample	NT	ELTs	[37]	[27]	[61]	[63]		[65]
Process (°C)	500	500	450	550	550	450	550	550
Proximate analysis (wt%)								
Moisture	2.1	1.0	0.37	-	3.57	1.5	1	0.9-1.14
Volatile Matter	0.0	1.5	7.78	-	12.78	3.1	1.2	2.9-3.5
Ash	9.9	9.5	8.27	15.2±0.2	15.33	16.0	16.5	14.3-13.6
Composition (wt%)								
Zn	4.06	3.73	6.68	4.2±0.3	-	-	-	-
S	2.51	2.67	1.9	2.0±0.1	-	-	-	-
Mg	0.06	0.07	0.147	0.1±0.02	-	-	-	-
Al	0.04	0.05	-	1.0±0.3	-	-	-	-
Si	0.29	0.31	1.69	1.6±0.2	-	-	-	-
K	0.12	0.08	0.0969	-	-	-	-	-
Ca	0.18	0.16	0.127	-	-	-	-	-
Ti	0.00	0.02	0.0171	1.3±0.2	-	-	-	-
Fe	0.03	0.03	0.0393	0.3±0.1	-	-	-	-

Zinc is originally present in the rubber as vulcanization activator, as inorganic filler in replacing the silica and/or as resulting from the galvanizing of steel reinforcing mesh which produces the iron. This element has been found in the range 3.73-4.06 wt% similarly to the values reported by Helleur (4.2±0.3wt%) [38] and below those reported by Conesa (6.68wt%) [37]. Silicon results more than five times lower than those reported in the literature [33, 34].

Heavy metals, such as nickel, vanadium, chromium, lead, detected in low concentrations in some reported testing [61], are not detectable in the obtained chars (<5 ppm).

In order to compare the char obtained at different temperature, the carbonaceous residue recovered after pyrolysis of NT at 400°C and 500°C has been subjected to scanning electron microscopy (SEM) and analysis of the elemental composition by EDAX probe. The micrographs resulting by observation of different site of interest, which allows to observe the morphology of the powders and their carbon-like consistency, are reported in Figure 3.13.

To reduce the punctual effect of the SEM-EDAX analysis, very sensitive to sampling, on each sample have been also subjected to XRF analysis. The obtained data are reported in Table 3.9. The data demonstrates that limited compositional differences are detectable in samples produced at 400 and 500°C therefore, in this range, the temperature affect significantly the degree of degradation but not the elemental composition of the degraded tires.

Table 3.9 - Elemental analysis of char produced at 400 and 500°C for NT.

Sample	NT			
	400		500	
Process (°C)				
Composition (wt%)				
	EDAX ^a	XRF	EDAX ^a	XRF
C+O	92,09	90,58	89,73	91,21
C	84,91	NR	85,70	ND
O	7,18	NR	4,02	ND
Mg	0,07	0,10	0,06	0,15
Al	0,27	0,07	0,66	0,06
Si	1,02	0,59	0,09	0,18
S	2,15	2,95	3,03	3,10
K	0,10	0,11	0,10	0,12
Ca	0,08	0,25	0,12	0,31
Ti	0,00	-	0,00	0,00
Fe	0,02	0,04	0,05	0,07
Cu	0,02	-	0,14	0,02
Zn	4,17	5,03	6,03	4,50
Br	-	0,08	-	0,11
P	-	0,08	-	0,06
Co	-	0,08	-	0,08
Al	-	0,07	-	0,06
Cl	-	0,04	-	0,04

^aAverage of 5 sites of interest.

ND – Not detectable.

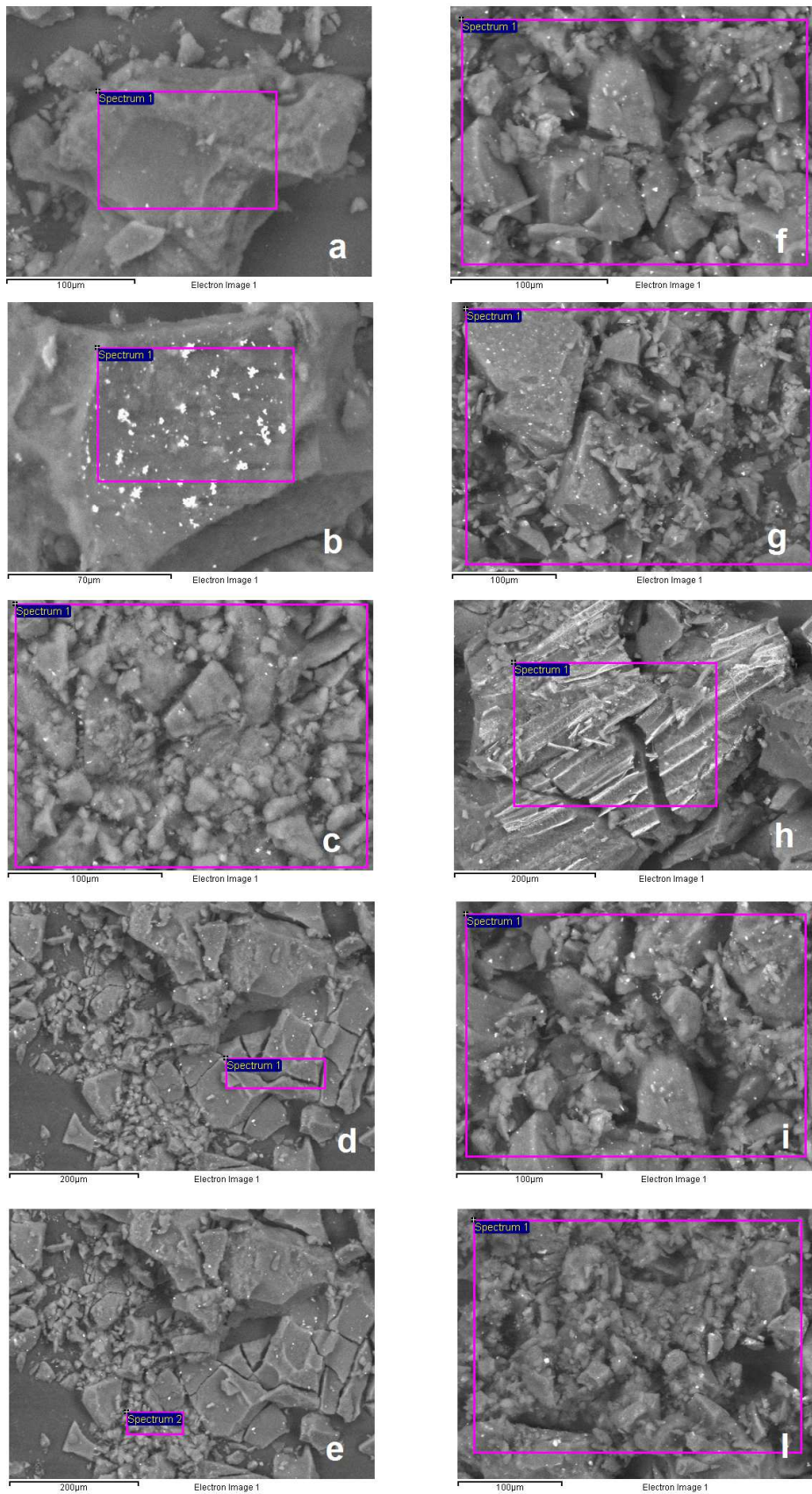


Figure 3.13 – SEM micrograph of different site of interest of chars derived from pyrolysis of tires at (a-e) 400°C and (f-i) 500°C.

The specific surface area, the elemental analysis and the calorific values, evaluate through ASTM D 1552-07, essential parameters for assessing the quality of the char, are reported in Table 3.10. In the solid samples produced by pyrolysis at 500°C remains 0.84 wt% (NT) and 0.87 wt% (ELTs) of sulfur with respect to the total weight of the pyrolyzed tires. The sulfur contents reported to the weight of the char fraction (2.51wt% for NT and 2.50wt% for ELTs) is similar to the average values reported by analogous processes (Table 5). The Gross Calorific Value (GCV) is over 32000 kJ/kg, higher than other char residues and this is mainly due to its higher hydrogen content. The specific surface area (SSA), amounting about 63 m²/g, is in line with literature data and could be increased considerably through specific activation processes to obtain active carbons [39].

Table 3.10 - Specific surface area (SSA), CHN-O/S analysis and calorific values of the chars produced at 500°C compared with literature data.

Sample	Process (°C)	Elemental composition (wt%)					SSA (m ² /g)	GCV (kcal/kg)	NCV (kcal/kg)
		C	H	N	O	S			
NT	500	86.40	3.10	0.30	4.43	2.51	63.1	7900	7800
ELTs	500	85.50	3.30	0.40	4.90	2.50	63.7	7900	7700
[8]	500	83.5	0.6	0.3	1.1	2.4	-	6979	-
[37]	450	88.19	0.60	0.10	-	1.90	93	-	7367
[39]	500	86.62	1.39	0.75	-	2.24	65.2	-	-
[61]	550	85.31	1.77	0.34	-	2.13	-	7336	-
[64]	550	-	-	-	-	-	55.5	-	-
[65]	550	95.9	0.5	0.2	<0.1	3.3	-	6831	-

In a corporate certificate from Standard on environmental management and quality (ISO 14001 and ISO 9001) such as Curti S.p.A., the storage and handling of the pyrolysis products must always be accompanied by the Material Safety Data Sheet (MSDS) of the product itself, as well as the related safety precautions.

Accordingly, a MSDS has been compiled according to the international standard requirements. Its translated version is reported in experimental part (chapter 4.2.6).

3.2.6. End-use for char

In Collaboration with LRCCP (*Laboratoire de Recherches et de Contrôle du Caoutchouc et des Plastiques* - French Rubber and Plastics Research and Testing Laboratory), a laboratory specialized in research, testing and consulting services in the field of rubber and

polymers, has been estimated the impact of the introduction of the char in a Natural Rubber (NR) compared with standard carbon blacks. This work, carried out within the framework of the BIOPROOF project, provides for the assessment of mechanical and dynamical properties of different formulations with char produced in this plant. The char has been produced by pyrolysis of truck (TT) and car (CT) tires at 500°C as set point temperature. No secondary treatment (such as grinding or powdering) has been performed on the pyrolysis solid residue unless mechanical separation of the metal from carbonaceous residue.

For each char (TT and CT), two kind of formulations have been tested:

- total substitution of standard carbon black by one char;
- blending 20/80 with 20% of produced char (TT or CT) and 80% of N330 standard carbon black.

The obtained results have been compared with those obtained with N660, N550 and N330 standard carbon blacks.

The mechanical properties obtained for each formula are summarized in Tables 3.11 – 3.14. Values of reference for each standard carbon black are presented. Properties of the best char tested currently in the BIOPROOF project and in the same conditions are added to compare the results.

3.2.6.1. Mechanical properties for total substitution with N660 as reference

Table 3.11 - Physical properties with N660 as reference on base 100 (total substitution).

	Reference N660	100% TT	100% CT	100% Pyroblack referent
Hardness Shore A	100	87	98	99
Strain				
Tensile strength	100	100	93	112
Elongation at break	100	128	100	112
M100%	100	65	95	74
M300%	100	47	83	76
M300/M100	100	72	86	102
Tear strength Delft	100	119	91	133
Angle tear strength	100	135	140	212
Compression set	100	78	88	81
Abrasion	100	74	82	104
FTFT	100	68	39	146

From the previously reported data it has been observed that:

- in comparison with N660, the CT char has about the same properties except for the modulus at important strain (M300%) and for fatigue and abrasion resistances which are decreased.
- Concerning the modulus 100 %, CT char is better than the Pyroblack reference.
- With the TT char the level of reinforcement is worst. Properties of compression, abrasion and fatigue resistances are also decreased for TT char compared to the references.

3.2.6.2. *Mechanical properties for total substitution with N550 as reference*

Table 3.12 - Physical properties with N550 as reference on base 100 (total substitution).

	Reference N550	100% TT	100% CT	100% Pyroblack referent
Hardness Shore A	100	87	97	99
Strain				
Tensile strength	100	101	94	113
Elongation at break	100	130	102	114
M100%	100	64	94	73
M300%	100	46	81	75
M300/M100	100	72	86	105
Tear strength Delft	100	130	99	145
Angle tear strength	100	145	151	228
Compression set	100	79	89	82
Abrasion	100	80	90	113
FTFT	100	69	40	148

From the previously reported data it has been observed that:

- when TT char is used in a total substitution and compared with N550, a poor reinforcement and fatigue behaviour is observed. Inversely, the elongation at break and tear properties are improved in comparison with N550 reference.
- For CT char, upon total substitution of N550, better properties are obtained compared to TT char except for tensile strength, tear strength Delft and fatigue resistance,.
- Hardness, elongation at break, M100 and tear strength Delft are not affected significantly. However, M300, compression behaviour, abrasion resistance and

fatigue resistance are decreased. Inversely, angle tear strength is improved. The reinforcement values obtained with the CT char are the best of all the chars studied in the BIOPROOF Project.

3.2.6.3. *Mechanical properties for total substitution with N330 as reference*

Table 3.13 - Physical properties with N330 as reference as reference on base 100 (total substitution).

	Reference N330	100% TT	100% CT	100% Pyroblack referent
Hardness Shore A	100	79	89	90
Strain				
Tensile strength	100	87	80	97
Elongation at break	100	127	99	111
M100%	100	60	88	69
M300%	100	39	69	64
M300/M100	100	65	78	92
Tear strength Delft	100	87	66	97
Angle tear strength	100	60	63	95
Compression set	100	90	101	94
Abrasion	100	63	70	88
FTFT	100	45	26	97

From the previously reported data it has been observed that:

- compared to N330, TT char degrade all properties with the exception of the elongation at break which is increased.
- Curti CT char doesn't impact elongation at break and compression set compared to N330. All the others properties are degraded. As with N550, except for fatigue resistance, better properties are noticed with CT.
- The level of reinforcement (for modulus) with CT char is again better than the reference char.

3.2.6.4. Mechanical properties for blending 20/80 with N330 as reference.

Table 3.14 - Physical properties with N330 as reference on base 100 (blending 20/80).

	Reference N330	100% Curti PL	100% TT	100% CT
Hardness Shore A	100	94	97	100
Strain				
Tensile strength	100	101	95	95
Elongation at break	100	109	99	96
M100%	100	93	97	98
M300%	100	83	93	98
M300/M100	100	89	95	100
Tear strength Delft	100	73	80	105
Angle tear strength	100	96	84	95
Compression set	100	112	109	112
Abrasion	100	99	97	131
FTFT	100	82	76	112

From the previously reported data it has been observed that:

- Blending 20/80 with TT char doesn't impact significantly strains properties (except for M300 which is inferior of N330 reference). Hardness, compression set, abrasion and fatigue resistance are slightly decreased. Only tear strength Delft seems to be influenced by this blending.
- Blending 20/80 with CT char doesn't impact strain properties and hardness. Tear strength Delft is less decreased than with TT char whereas angle tear strength is more degraded for CT char.
- In comparison with the reference pyroblack, the reinforcement properties and break properties are about the same. The tear properties and the fatigue properties are degraded.

3.2.6.5. Dynamical properties

The dynamic properties have been evaluated by Rubber Process Analyzer (RPA) with strain sweep from 0,1 to 100 % at 50°C and plotted in Figure 3.14. This analyses allow to estimate the Payne effect.

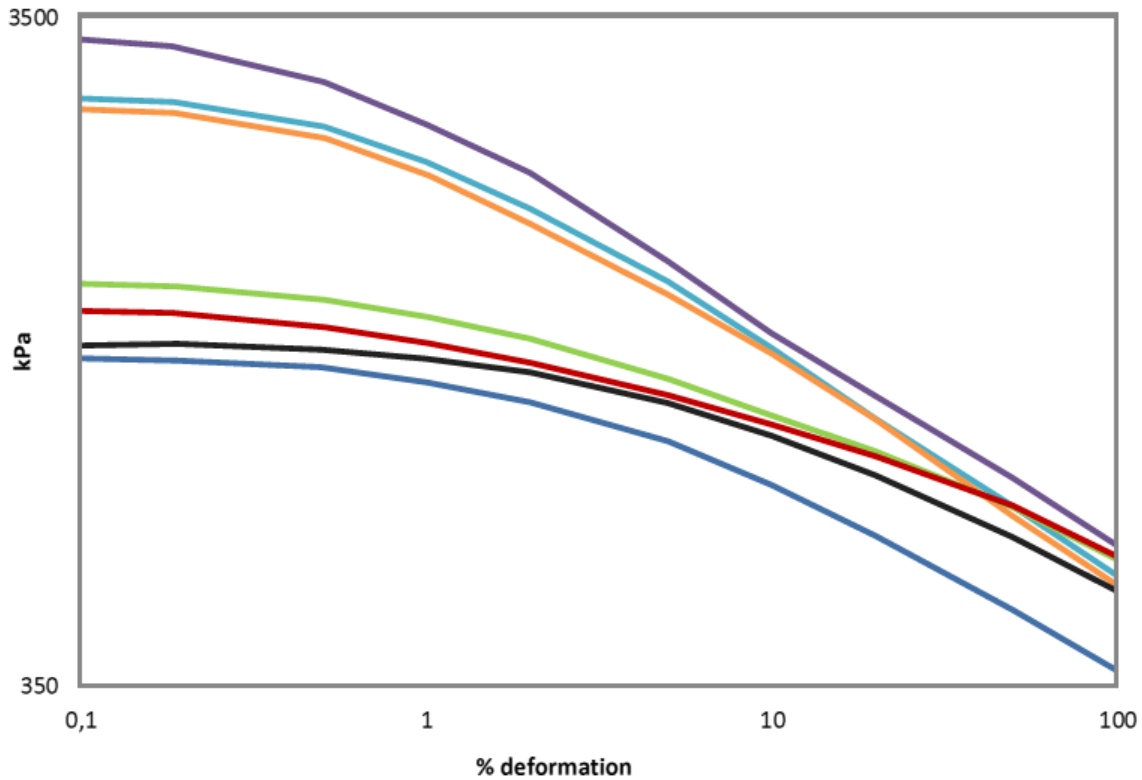


Figure3.14 - Curves RPA of compounds with TT and CT chars. (—) Reference N330; (—) 20/80 VL/N330; (—) 20/80 PL/N330, (—) Reference N660; (—) Reference N550; (—) 100% CT; (—) 100% TT.

From the previously reported data it has been observed that:

- with 100% of TT char, dynamic behaviour is clearly inferior of the three references (blue curve). CT char (black curve) behaves differently, and somehow closer to reference N550 (red curve).
- The curves confirm the better level of reinforcement with CT as with TT char.

In conclusion, the effect of applying the chars obtained at 500°C with Car and truck tires in the pilot plant in the reinforcements of rubber materials can be summarized as follows:

- from a general point of view, the TT char degrades strongly the mechanical and dynamic properties of the formulation. The quality of reinforcement is hence really impacted (even compared to a standard carbon black N660).
- The CT char seems to be more performing than TT, with a very good level of reinforcement (regarding the modulus) close of the level of standard carbon black semireinforcing as N660 or N550. It is even better than the char referent of the BIOPROOF project.

- When Curti char is blended with a commercial analogue char, such as N330, in 20/80 proportion, mechanical properties are close to those obtained with the N330, principally for strains properties.
- The dynamic analysis confirms this tendency in 20/80 proportion, with a behaviour close to N330 and better for CT char.
- Compared to the best char currently tested in the BIOPROOF project, the chars produced in this pilot plant impact more onto tears and compression set properties and also onto fatigue and abrasion resistances when compared to the reference char for a blending 20/80 with N330.

3.2.7. Design of a continuous industrial pyrolysis plant

The experimentation have demonstrated that pyrolysis is an efficient and profitable process for the disposal of end-life tires.

For this reasons, also considering the statements of intent of some companies in the use of pyrolysis products, the technology applied in the pilot plant has been up-scaled to a continuous plant.

The innovative elements brought by the proposed technology are:

- processing of whole tires or cutted in a half tires with significant savings in terms of:
 - initial investment;
 - maintenance;
 - staff;
 - management
- supply and discharge of solid materials through hydraulic seal which involves the possibility to operate while maintaining all of the following operating modes:
 - continuous cycle;
 - guarantee anti-infiltration, increasing the safety of the process.

In first instance, in order to scale-up the reactor, have four possible configurations been considered, all of them enabling the use of the hydraulic seal:

- A. continuous system with electric heating;
- B. continuous system with internal syngas heating;
- C. discontinuous system with three vertical reactors and internal syngas heating;
- D. discontinuous system with three vertical reactors and external heating with combustion fumes.

Table 3.15 - Key features of different pyrolysis reactor configurations.

Solution	Reactor complexity	Flexibility (reliability for failures and still)	System control and setting	Thermal distortions in the reactor
A	HIGH Conveyor belt inside, large reactor	LOW A fault in the loading or unloading tape generates a plant shutdown	EASY The resistors allow easy adjustment and uniformity of the ongoing process	LOW The resistors allow uniformity of heating and easy control
B	HIGH Conveyor belt inside, large reactor	LOW A fault in the loading or unloading tape generates a plant shutdown	MEDIUM Continuous process but managed with hot gases in the room	HIGH The tape and the release of hot gases behave phenomena hot - spot dangerous
C	LOW only opening and closing valves, without the need for sealing	GOOD It is possible to stop and isolate one of the three reactors	VERY DIFFICULT Managing of three plants discontinuous	MEDIUM Possibility of hot spots and thermal fatigue cycles
D	LOW only opening and closing valves, without the need for sealing	GOOD It is possible to stop and isolate one of the three reactors	DIFFICULT Managing of three plants discontinuous but simple heating management in case of emergency	--

From the consideration reported in Table 3.15, it was found that solution D brings major benefits in terms of reduced operating costs, reduced stopping risk and system flexibility. Moreover, similar plants for pyrolysis of tires are already operating.

The project of the continuous pilot plant considers to include as key actor:

- Consortia administering EPR in national EU countries, which can critically contribute to the dissemination of the technology and which are distributing the contributions for treatment;
- tire producers, which will be interested in endorsing a technology that reinforces the sustainability of their product's lifecycle.
- Research institutes, to propose research lines to improve the process and the products;
- public authorities, which will be interested in supporting an innovative recycling technology;

- local communities of the places where the new plants will be installed, that will need to be reassured on the absence of risks for health and quality of life due to the plant.

The action target groups will be the following:

- tire recyclers, i.e. companies engaged in the business of collecting tyres and treating them to recover materials. At the EU level, they are grouped in ETRma, and there are national bodies as well (in Italy, they are federated through ECOPNEUS, ECOTYRE and similar bodies)
- Purchasers of recycled materials, i.e. steelmakers (for steel) and chemical companies (for char).

The main performance of the plant pyrolysis expectations for the pyrolysis system in version 1.5 t/h (TPP1.5) and 4t/h (TPP4) and of the products obtained by the process are reported in Table 3.16.

The plants, projected as represented in Figure 3.15 and 3.16, is also profitable, showing a high return on investment and a breakeven is reaching after 4 years from plant setup.

Results and discussion

Table 3.16 – Main continuous plant performance expectations.

	TPP1.5	TPP4	Units
Treatment capacity			
Hourly amount	1.5	4.0	t/h
Annual operation	7500	7500	h/a
Annual treatment capacity	11250	30000	t/a
Output			
Char	3543.75	9450.00	t/a
Oil	2989.13	7971.00	t/a
Steel	1462.50	3900.00	t/a
Electric-powered	937.50	2812.50	MW h/a
Plant dimensions			
Area	11000	15200	m ²
Height	17	19	m
Autonomy			
Operating autonomy	14	14	gg
Plant consumption			
Electric-powered	0.346	0.644	MW h
	2593.28	4830.91	MW h/a
GPL	4720.69	11801.73	kg/a
Water	15812.5	42625.00	m ³ /a
Baking soda	30.00	78.00	t/a
Nitrogen	3000	4500	m ³ /a
Diesel oil	45	90	m ³ /a
Urea	15	39	m ³ /a
Atmospheric emissions			
Combustion gas flow rate	4.60	11.96	kg/s
	12170.00	322842.00	t/a
Estimated NO _x	70	70	mg/Nm ³
	6.74	17.52	t/a
Estimated SO _x	10	10	mg/Nm ³
	0.96	4.16	t/a
Estimated CO	30	30	mg/Nm ³
	2.89	7.51	t/a
Estimated CO ₂	30863.25	82302.00	t/a
Ash	3	3	mg/Nm ³
	0.29	0.75	t/a
Noise impact			
Noise impact (based on the acoustic zoning)	80	80	dBa

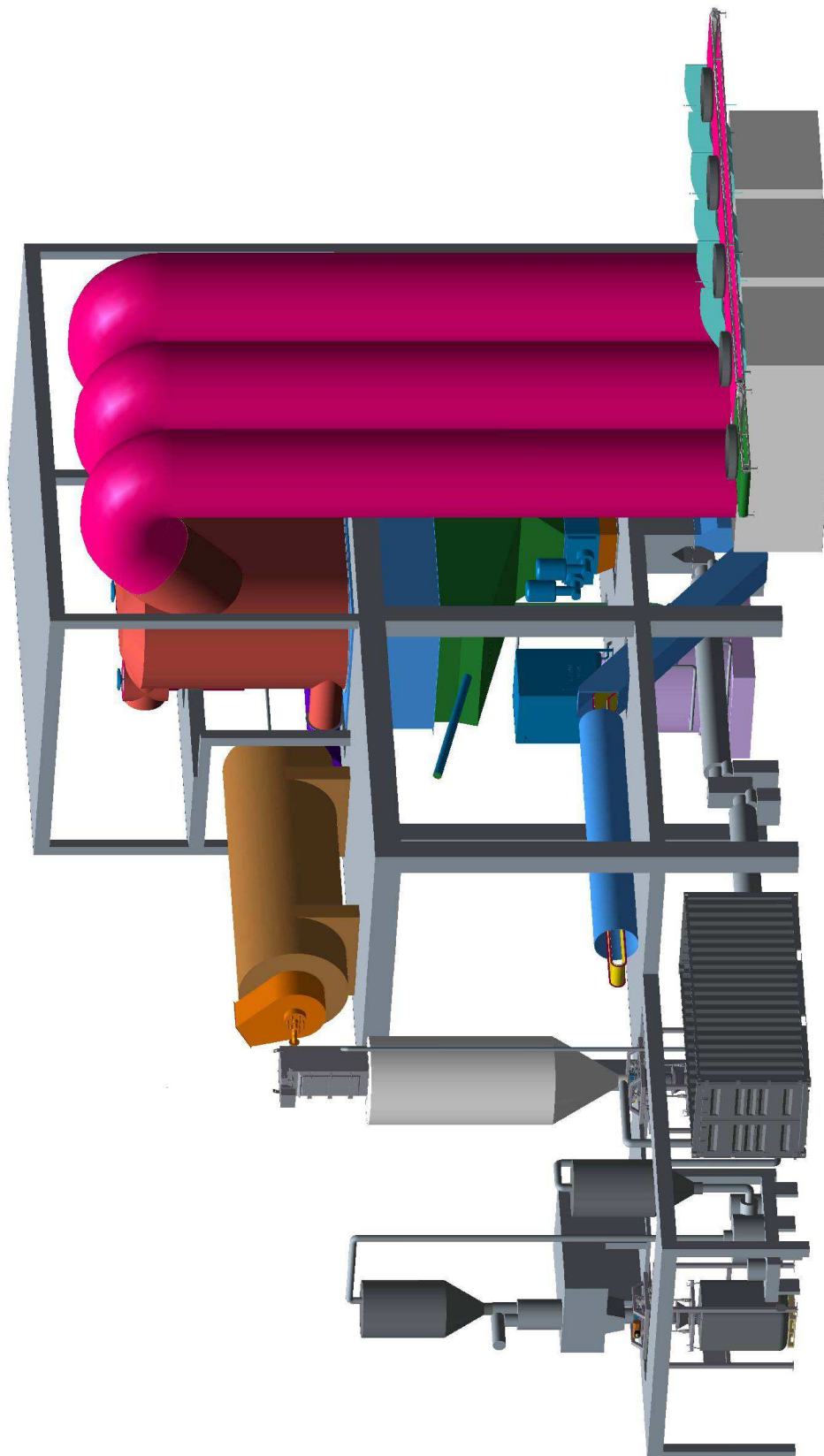


Figure 3.15 - Layout of the continuous industrial reactor with the loading and unloading systems.

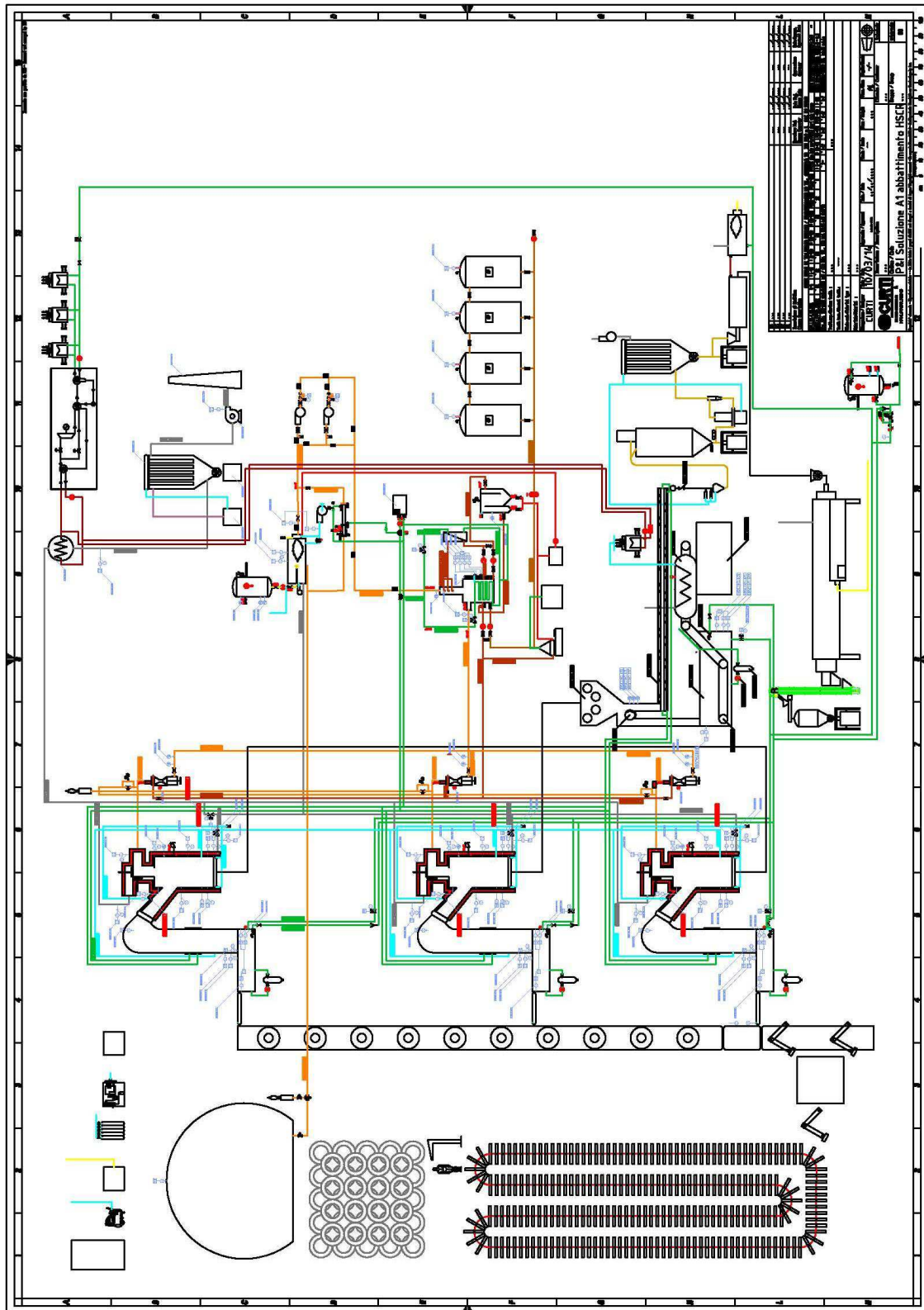


Figure 3.16 - Temporary diagram of the continuous industrial plant.

3.2.8. Conclusions

The pyrolysis of new and end-life tires have been successfully carried out conducted in presence of steam in an innovative pilot plant which is able to process whole tires, thus saving the energy costs of shredding, and simultaneously allows energy and materials recovery. By conducting the pyrolysis above 450°C, the process gets:

- an oil fraction rich of high commercial value compounds, with high GCV and low sulphur content (1wt%). The characterization of the oil fraction, repeated after one year, shows negligible changes during this period.
- A syngas fraction enriched with hydrogen and methane;
- a char fraction (40wt%) with high GCV and promising specific surface area;
- a steel fraction, completely recoverable through specific recovery chains.

The oil fraction contains important amount of BTX which allow the use of the lighter fractions as a source of high value chemicals after distillation process.

Both the oil and syngas fractions can be used to completely sustain the process with a energetic surplus. In this plant, which is not optimized for the energy saving and recovery, the energetic surplus can be estimated in 337MJ/batch.

The characterization has shown that the solid residue may be used as fuel, thanks to its high GCV, or as a secondary raw material in blends with standard carbon black for the production of rubber compounds for technical sectors. Specific tests have shown that the use of non-shredded char in 20/80 blends with N330 carbon black does not affect the mechanical properties of the compounds obtained with the N330, principally for strains properties.

As said before, the CT char is the most interesting char considering the reinforcement properties. There are big differences between the level of reinforcement of char obtained from car and truck tires. Preliminary data obtained after grounding down chars at 10µm demonstrates that the properties of the blended compounds can be further improved. Moreover, realization of blending in other matrices like for example EPDM will be thorough.

In summary, the study has shown that is possible to produce steel and char as secondary raw materials in a completely self-sustained process. For this reason, the results of the pilot experimentation, the regulatory, informative and cultural barriers, and considering the cases of the plants started in Italy in the last years have been taken into account in the design of a continuous multi-batches plant able to process from 1.5 to 4.0 tonnes per hour.

The project aims to implement the first industrial application and actions for market replication, of an innovative technology for the treatment of ELTs, capable of improving the quality of recycled materials. The technology is characterised by the following elements:

- an innovative pyrolysis based treatment for ELTS, characterised by high efficiency and sustainability, and capable of recycling 100% of ELTS into char, steel, oil and syngas;
- the capacity to obtain intact steel fibres from ELTS and so characterized by high quality. The residual steel obtained through mechanical process is recovered in shredded form and thus has a low market value with respect to that obtained after pyrolysis of whole tires. Furthermore, the absence of grinding processes minimizes the surface oxidation processes that compromise the quality of the steel.
- High replicability and market uptake potential of the technology, due to the small scale of plants, and their reduced environmental and social impact.
- Lower energy consumption compared to continuous processes with grinding pre-treatment of tires.

3.3. Pyrolysis of Carbon Fibers Reinforced Compounds [66]

The preliminary part of this work is aimed at the recovery of carbon fibers from composites and prepregs via pyrolytic degradation of the resin component. To better understand the real recovering capability of the process, both uncured materials (prepreg) and cured composites (Figure 3.17), supplied by Ri-Ba Composites srl, have been pyrolyzed. Both kinds of tested samples were scraps coming from different stages of the manufacturing process.



Figure 3.17 - Typical prepregs with LDPE protective film (a) and typical cured scraps of thick carbon fiber composites (b) [66]. Reproduced by permission of Wiley.

The prepregs are cutouts of carbon fibers' fabrics, impregnated with uncured B-staged epoxy resin and protected with a 12wt% of thin film of low density polyethylene (LDPE) on both sides (Figure 3.17a). The resultant total thickness of each sheet does not exceed few millimetres. The cured samples are scraps and rejects of thick composites constituted of up to 70 layers of prepregs with a total thickness of about 3 centimetres (Figure 3.17b).

3.3.1. Characterization of feed materials

In order to set up conditions for pyrolysis experiments, a preliminary thermogravimetric investigation of cured and prepreg samples has been carried out in dynamic mode and inert atmosphere. The thermograms reported in Figure 3.18 show degradation to start at around 300°C, namely T_{onset} for thermal degradation is 371°C for prepregs and 377°C for cured scraps. While for the cured composite thermal degradation proceeds with a single stepwise weight loss leading to a constant weight residue (69%) after 600°C, TGA of prepreg displays a two-step degradation pattern, where the degradation processes are quite overlapped. The solid residue

(58%) is lower than in the cured composite and this overall behaviour can be safely attributed to thermal degradation of not only the resin fraction but also of the covering LDPE-based films. Given TGA results, the range 450-600°C has been selected for pyrolysis experiments: different tests have been performed every 50°C.

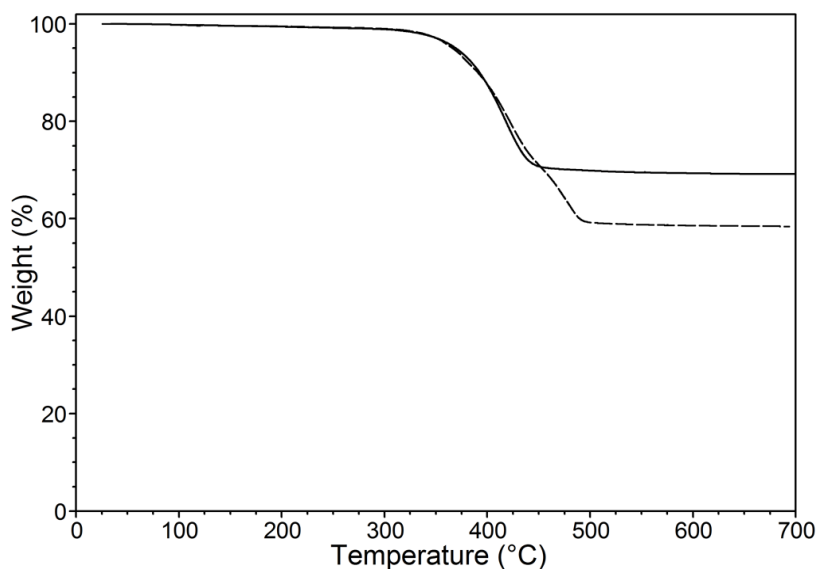


Figure 3.18 - TGA thermograms of preregs (---) and cured scraps (—) in nitrogen atmosphere [66]. Reproduced by permission of Wiley.

Since literature reports [67] that the presence of polyethylene leads to the formation of waxes which could condense at low process temperature, pyrolytic test on preregs at 450°C process temperature were not performed to avoid pipeline obstruction.

Once suitable temperature ranges have been identified, pyrolysis experiments have been performed in a batch pilot plant from Curti S.p.A [54], where each raw material load is about 70kg.

3.3.2. Pyrolysis yields

The pyrolytic process on cured composites or preregs has led to three main products streams, i.e. a gas phase, an oil fraction and a solid residue. The relative ratios depend on the reaction conditions applied (such as temperature and residence time). After determining the optimal residence time for the materials to be 2.5 hours, of which the effective pyrolysis step takes only about 20-30 minutes to complete, different temperatures have been tested. Figure 3.19 shows the yields of the obtained solid residue, oil and gas (the latter calculated by

difference) after pyrolysis of both prepregs and cured scraps as a function of the reaction temperature.

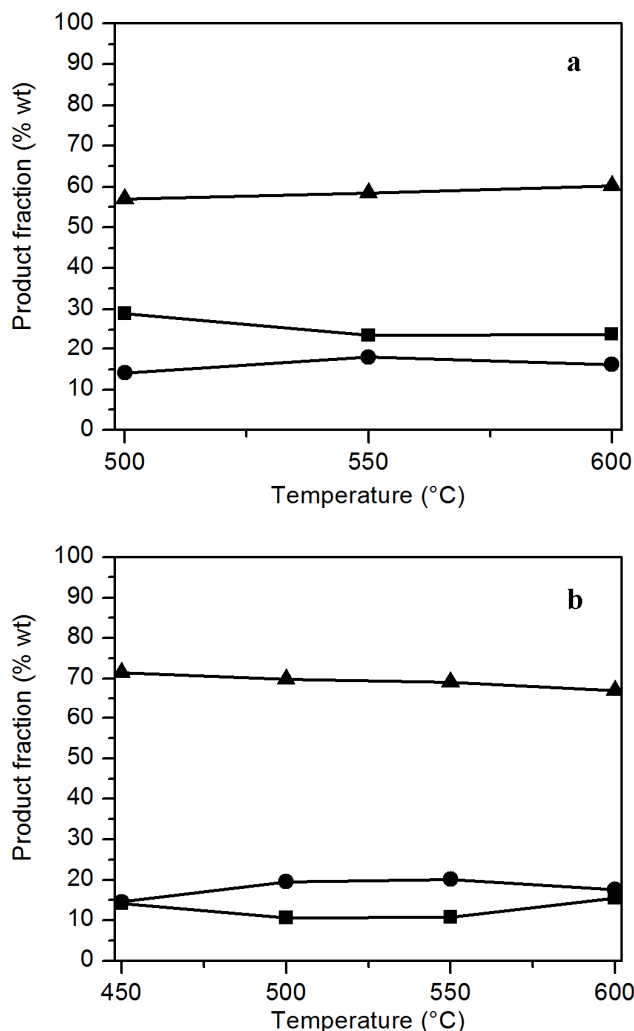


Figure 3.19 - Products distribution at different pyrolysis temperature for (a) prepregs with 12wt% of LDPE protective film and (b) cured CF composites. (▲) Solid residue; (■) Syngas; (●) Oil phase [66]. Reproduced by permission of Wiley.

It is noteworthy that at minimum and maximum applied temperature, the cured polymeric matrix decomposition leads to the formation of an almost identical amount of oil and syngas (oil/syngas ratio 1.0 at 450°C and 1.1 at 600°C) while, at intermediate temperatures (500-550°C), the amount of oil is almost double the gas production.

On the contrary, uncured epoxy polymeric matrix with LDPE films leads to the formation of 14.1 and 16.1 wt% oil fraction at minimum and maximum temperature

respectively with a maximum of 18.0 wt% at 500°C. The oil/syngas ratio increases from 0.5 to 0.9 when the temperature rises from 500 to 600°C.

3.3.3. Oil characterization

The volatiles condensed within the cooling system have been recovered at the end of each run in order to determine their composition. GC-MS analysis of the pyrolysis oils obtained at different temperatures for prepregs and cured scraps shows in all cases a complex mixture of organic compounds among which: benzene and its alkyl derivatives such as xylenes, toluene, ethylbenzene, ethylmethylbenzene, cymenes and 1,3-diisopropenylbenzene; phenol and its alkyl derivatives such as 2-methylphenol, 4-methylphenol and 3-ethylphenol; some linear and branched alkenes up to C₁₄, e.g. 2-methyl 2-butene, 2,4-dimethyl hexene, 1-decene and 5-tetradecene. Some aromatic heterocyclic compounds have been also detected, such as benzofuran and its alkyl derivative 2-methyl benzofuran, as well as disubstituted indanone derivatives.

Among such a complex mixture, benzene, toluene, xylene, ethylbenzene (BTXE) and styrene are of particular interest owing to their high market value as a source of light aromatics; besides, they are normally considered pyrolysis markers, hence their quantification has been carried out for each batch and the results are reported in Table 3.17.

Table 3.17 - BTXE and styrene content (g/l) in oils obtained by pyrolysis of prepreg and cured scraps at different temperatures [66].

Oil components	Process Temperature (°C)						
	Prepreg			Cured			
	500	550	600	450	500	550	600
Benzene	1.7	4.9	4.1	1.6	-	-	1.8
Toluene	3.4	7.5	7.5	1.7	1.9	3.6	5.8
Ethylbenzene	1.5	1.8	1.0	1.3	0.8	3.2	1.2
p-xylene	2.0	2.4	2.9	1.0	2.8	2.2	3.4
Styrene	1.0	1.3	1.5	0.6	0.7	0.7	1.2

In the case of cured scraps pyrolysis, the percentage of the compounds of interest grows with the process temperature in the 500-600°C range, reaching the maximum registered value of 13.3 g/l. For prepreg series, the maximum concentration of BTXE and styrene compounds is registered in the oil produced at 550°C and corresponds to 18.0 g/l, probably because of the presence of Polyethylene film that increases the pyrolyzable absolute fraction. The observed

trend with increasing process temperature is also reported for the oil obtained upon tires pyrolysis [8] and is attributed to secondary reactions that proceed via dehydrogenation or recombination during thermal degradation. In order to ensure any potential commercial value to the pyrolysis oils, possible contamination from heavy metal elements or other contaminants deriving from the complex systems used as raw materials, have to be ruled out. For this reason the oils produced via pyrolysis of both prepregs and cured scraps at different temperatures have been analyzed by XRF; the results are reported in Table 3.18 together with their density and viscosity.

Table 3.18 - XRF analysis of the oils obtained by pyrolysis of prepreg and cured scraps at different temperatures (wt%) [66].

Oil contaminants	Process Temperature (°C)						
	Prepreg			Cured			
	500	550	600	450	500	550	600
S	0.18	0.03	0.02	0.12	0.10	0.06	0.02
Si	0.14	0.03	0.03	0.02	0.04	0.02	0.03
Cl	0.08	0.05	0.09	0.08	0.05	0.09	0.08
Zn	0.21	-	-	-	-	-	-
Mg	-	-	-	-	0.03	-	0.03
Characteristics							
Density (g/cm ³)	1.040	1.048	1.071	1.050	1.063	1.071	1.077
Viscosity (cSt)	66.1	43.8	57.9	63.7	81.7	73.0	64.2

As shown in Table 3.18, all the oils contain a low amount of sulfur: when the pyrolysis temperature is $\leq 500^\circ\text{C}$ the sulfur content is between 0.10 and 0.18wt%, while the fraction is strongly reduced down below 0.06%wt when $T \geq 550^\circ\text{C}$. Silicon and chlorine are always well below 0.1%wt. Hence, the low content of sulfur and halogens, and the total absence of heavy metals make the obtained pyrolysis oils suitable as fuel without the need for any further purification process.

As a guideline for assessing the sustainability of the process, it can be observed that, stemming from the previously discussed data, the calorific value of the overall by-products, other than solid residue, obtained for example by pyrolysis of cured scraps at 500°C , can be roughly estimated in 242 MJ/batch, based on the actual composition and the associated calorific characteristics of each component as from the literature [68]. In the same conditions the pyrolysis pilot plant used for the present work has an average power consumption of 324

MJ/batch. However it is worth pointing out that the pyrolysis tests presently discussed were carried out in a demonstrative pilot plant that was built in order to investigate only the feasibility of the process for recovery and reuse of carbon fibers. Hence no particular attention was paid to the optimization of the energy balance, using for example electrical resistance elements as heating sources, instead of valorising the calorific properties of the pyrolysis by-products. This approach is mainly justified from the need to recover all the pyrolysis products to evaluate them and characterize the composition of all the products' streams. Nevertheless these by-products can sustain about 75% of the process energy requirement and these observations pave the way to the possibility of an optimized pyrolysis plant that, via the necessary changes and tuning in the scaling-up, might reach a complete self-sustainability of the process.

3.3.4. Syngas characterization

The gas mixture produced by pyrolysis of both cured and prepreg samples has been analyzed online on the plant, in order to correlate the volatile composition with the applied pyrolysis conditions. The recorded values are plotted in Figure 3.20 (prepregs) and 3.21 (cured scraps). The measured gases are H₂, CH₄, CO, CO₂, ethylene and ethane. C₃ is the sum of propane and propylene while C₄ is the sum of 1-butene, n-butane, 1,3-butadiene and isobutylene. The sum of other indeterminate incondensable species is named "Others".

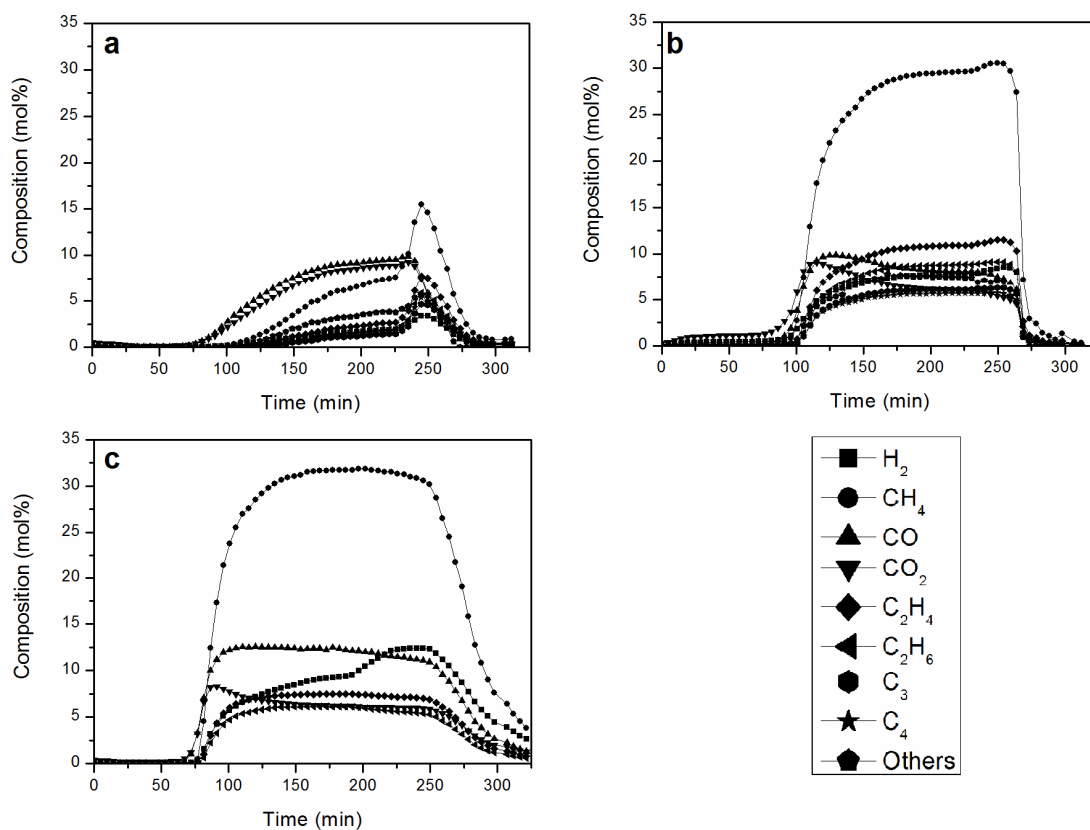


Figure 3.20 - Composition of the syngas during the run at (a) 500°C, (b) 550°C and (c) 600°C with prepregs with 12wt% of LDPE.

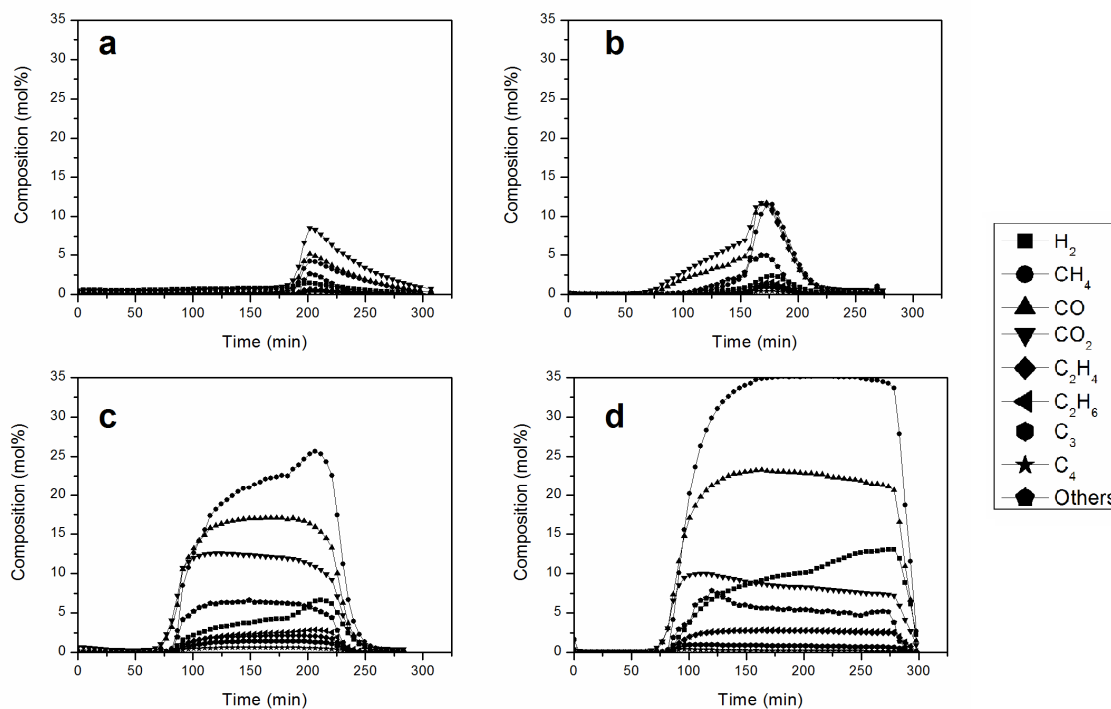


Figure 3.21 - Composition of the syngas during the run at (a) 450°C, (b) 500°C, (c) 550°C and (d) 600°C with cured scraps.

The average compositions of the syngas produced during the different pyrolytic experiments are reported in Table 3.19 and Figure 3.22. In addition, Gross Calorific Value (GCV) of each mixture at 1 atm and 288 K is presented in Table 3.12.

Table 3.19 - Chemical composition and GCV of the gas produced by pyrolysis of prepreg and cured scraps (%vol) upon modification process temperature [66].

Syngas components	Process Temperature (°C)						
	Prepreg			Cured			
	500	550	600	450	500	550	600
H ₂	4.9	7.7	12.9	6.0	5.0	6.9	11.6
CH ₄	23.0	29.3	37.9	17.6	22.3	32.2	38.7
CO	16.0	14.1	15.5	21.3	25.5	25.1	25.9
CO ₂	15.0	12.9	9.0	35.5	28.2	19.6	10.5
C ₂ H ₄	10.5	10.1	8.9	2.8	2.7	3.1	3.1
C ₂ H ₆	8.0	7.9	7.0	2.6	2.9	3.5	3.2
C ₃	6.2	5.7	3.3	2.2	1.8	2.0	1.0
C ₄	7.3	5.4	2.3	1.1	0.8	0.9	0.3
Other	9.1	6.9	3.2	10.9	10.8	6.7	5.7
GCV (MJ/Nm ³)	45.5	43.4	37.7	27.5	29.1	30.4	31.0
GCV (MJ/kg)	35.7	36.6	37.2	22.3	24.3	27.1	31.3

It is worth noting that different syngas produced by pyrolysis of prepreps or cured scraps at the same temperature are composed of comparable amount of hydrogen and methane while C₂, C₃ and C₄ fractions are higher for prepreps, possibly owing to thermo-degradation of the LDPE fraction. Furthermore they both contain high fraction of carbon oxides, generated from the breakdown of oxygen-rich moieties occurring in the resin formulation. By increasing the batch temperature, a reduction in oxides content is registered, mainly due to a decrease of the carbon dioxide component. Moreover, a decrease in concentration of heavier molecular weight compounds and a simultaneous increase of lighter species, in particular methane and hydrogen are observed. This trend, observed both for prepreps and cured composites and reported by other authors for the decomposition of analogous [43] and different materials [8], can be related to further cracking of evolved volatile matter at elevated temperatures.

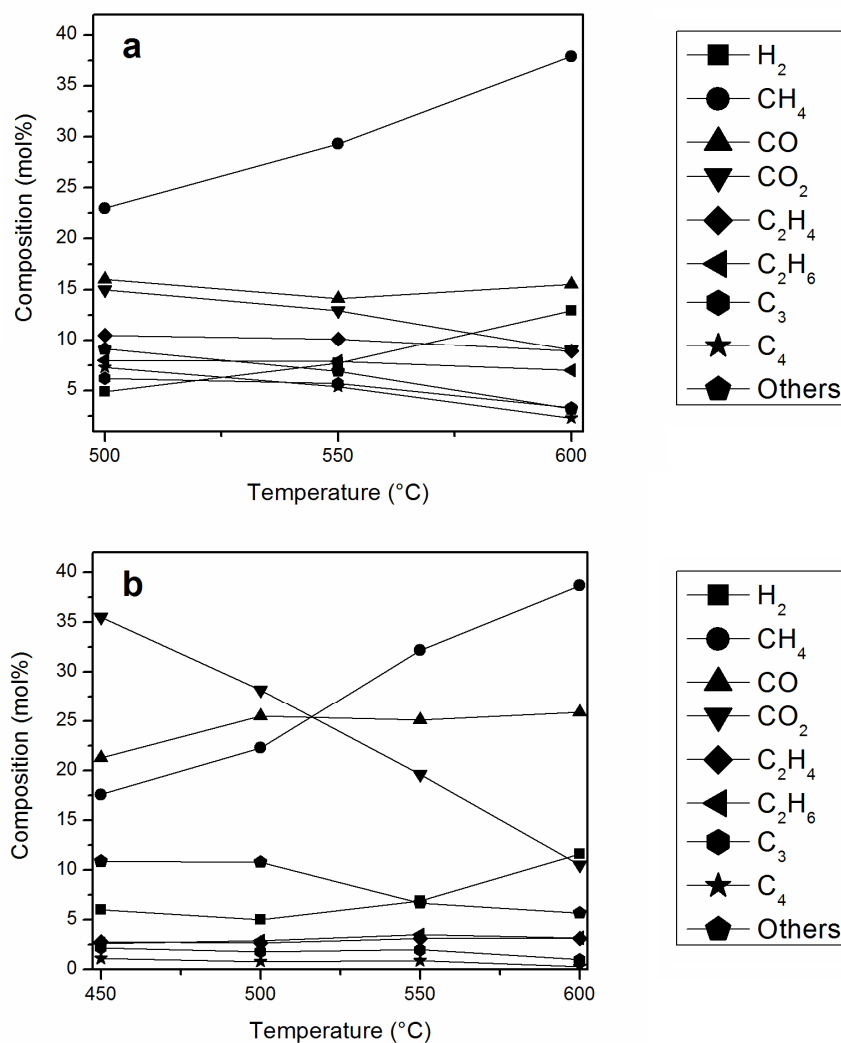


Figure 3.22 - Trend of the chemical species of the syngas as a function of temperature: (a) prepregs with 12wt% of LDPE protective film and (b) cured CF composites.

Finally, as reported in Table 3.19, the GCV increases slightly with process temperature for prepreg series (from 35.67 to 37.21 MJ/Nm³) and more significantly (from 22.25 to 31.25 MJ/Nm³) for cured scraps. This trend is mainly due to the reduction in the carbon dioxide fraction in the pyrolysis gas mixture caused by the increase of the process temperature.

3.3.5. Solid residue characterization

All the materials not volatilized and taken away during pyrolysis, either as gas or as condensable oil phase, at the end of the process have been recovered as a solid blackened residue which, at first sight, should be mainly composed of carbon fibers covered by a carbonaceous layer.

The total amount of solid residue left after the pyrolysis of cured scraps shows just a slight decrease from 71.4 to 67.0% when the temperature goes from 450 to 600°C. The company that provided the composites scraps stated an average 37% resin fraction in the composite before curing that, however, is significantly lowered owing to the loss of resin during the compaction under vacuum curing (see the 69% TGA solid residue discussed above). Moreover, should be considered the significantly high thickness (up to 35mm) of the processed multilayer scraps which can lead to diffusion problems along the depth of the materials which slows down the pyrolysis of the resin in the inner layers, thus increasing the fraction of solid residue with respect to what expected. Upon raising the process temperature, the decomposition of the inner layers resin is boosted, thus decreasing the extent of the solid residue.

On the contrary, the total amount of solid residue left by the prepreg pyrolysis shows an increment from 57.0 to 65.7% when the temperature increases in the 500-600°C range. Since the PE component accounts for roughly 12 wt% of the loaded raw material, the pyrolytic solid residue yield of resin composite alone can be estimated around 60% (see the 58% TGA solid residue discussed above). The increasing quantity of solid residue could be attributed, among other factors, to the formation of higher proportion of coke like material as a product of secondary re-polymerization reaction of volatile degradation fragments as reported by other authors for both epoxy resin [68] and polyethylene [33]. However, owing to the fact that real production wastes of different nature are used for the present work, it is worth to point out that the actual fiber to resin ratio may also vary from a batch to the other, so the solid fraction cannot be taken as an absolute parameter to judge the pyrolytic performance.

Far more interesting is the analysis of the aspect shown by this solid residues, i.e. carbon fibers. In Figure 3.23 SEM micrographs of some dry virgin carbon fibers and of fibers obtained in the different pyrolysis conditions are reported.

Virgin fibers (Figure 3.23a) appear, as expected, smooth and homogeneous. All CFs obtained from prepreps pyrolysis (Figures 3.23b to 3.23d) appear well separated, but single fibers display some traces of inhomogeneous materials coating the surface. In the solid residues obtained from cured composites, sampled from the inner layers of the starting thick scraps, CFs obtained at lower temperatures (450 and 500°C, Figure 3.23e and Figure 3.23f respectively) clearly display resin traces that stick the fibers together in bundles. At higher temperatures (550 and 600°C, Figure 3.23g and Figure 3.23h respectively), instead, residual resin is far less evident, and fibers appear well separated and mainly covered by a thin carbonaceous layer.

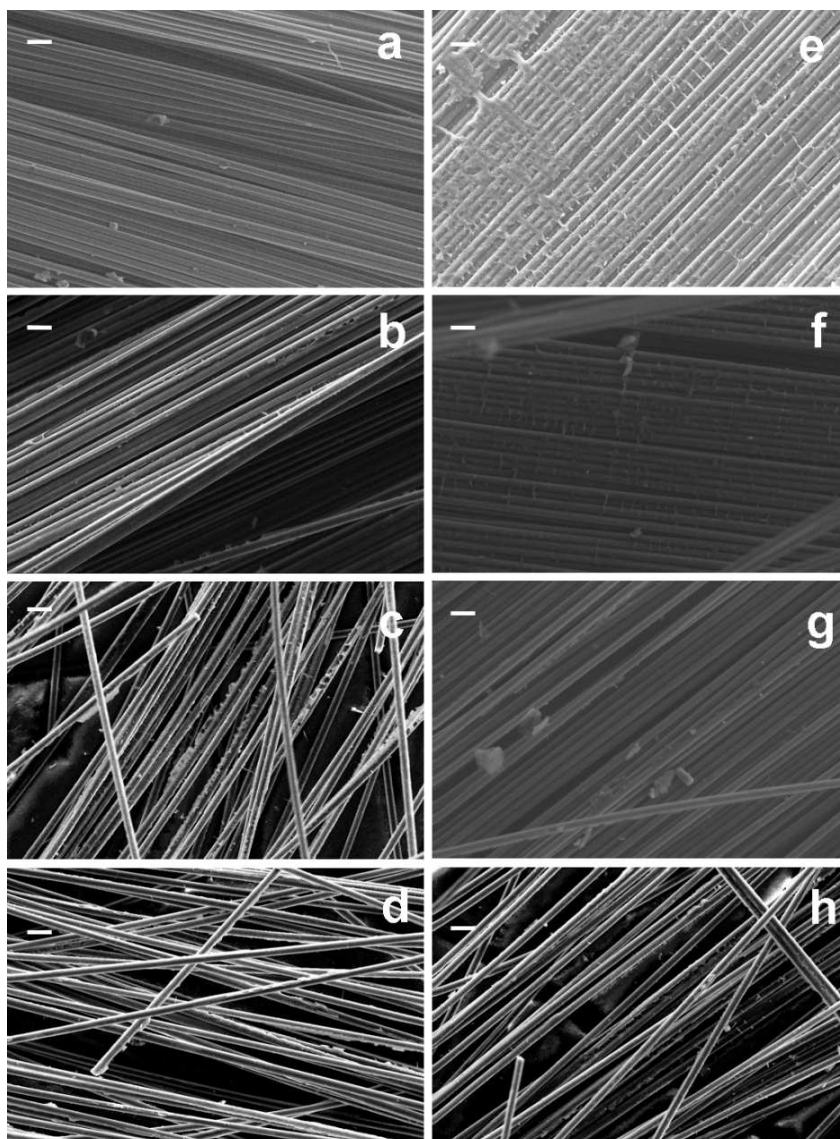


Figure 3.23 - SEM micrographs of (a) virgin carbon fibers, (b-d) carbon fibers recovered from prepregs pyrolysis at 500, 550 and 600°C, and (e-h) cured pyrolyzed CFRPs at 450, 500, 550 and 600°C [66]. Reproduced by permission of Wiley.

With the aim to remove this outer carbonaceous layer covering the fibers surface, the solid residues obtained from the pyrolysis of cured scraps at 500 and 600°C have been subjected to an additional oxidation step. Accordingly to the literature [22], two different oxidation temperatures will be considered for the process, namely 500°C for fibers obtained in the pyrolysis batch carried at 500°C and 600°C for fibers obtained in the batch at 600°C, so that the two most extreme process conditions can be analyzed.

Figure 3.24 shows TGA runs carried out in air in isotherm condition at 500 and 600°C respectively with the aim of understanding the optimal conditions for the additional oxidizing process.

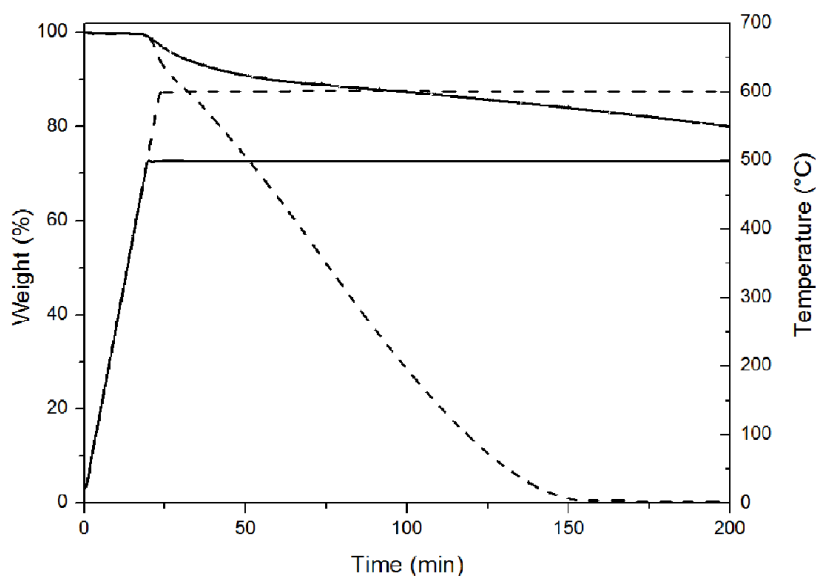


Figure 3.24 - TGA thermograms of cured scraps pyrolyzed at 500°C, isotherm at 500°C in air (—) and cured scraps pyrolyzed at 600°C, isotherm at 600°C in air (···) [66]. Reproduced by permission of Wiley.

The thermogravimetric analysis in oxidizing atmosphere demonstrates that some degradation starts when reaching 450°C for both samples, irrespective of the previously applied pyrolytic batch conditions. If the temperature is kept constant at 500°C, after 30 minutes the sample burns out about 9% of its initial weight. Increasing the residence time, the sample shows a substantially constant weight loss of roughly 0.1 %/min. If the temperature is kept constant at 600°C, only 5 minutes are required to reach the same weight loss of 9.1%. Increasing residence time up to 85 minutes, the sample shows a weight loss equivalent to 0.8 %/min and the degradation of solid pyrolysis residue results complete after 130 minutes.

Figure 3.25 shows SEM images of fibers oxidized in a muffle oven at 500 and 600°C for 10, 20, 30, 40, 50 and 60 minutes respectively.

When the oxidation was carried out at 500°C, at least 40 minutes are required to completely remove evidence of resin residue. For shorter oxidation times, in fact, the residual resin connecting the fibers clearly appears (Figure 3.25a-10/3.25a-30) and this macroscopically results in stiff CFs mats, as the untreated ones. After 40 minutes of mild oxidation (Fig. 3.25a-40) the resin was completely removed: the carbon fibers surface appears uniform and not affected by pitting or any other surface damage and they are not connected anymore by the resin and tend to easily separate. Longer process times (Figure 3.25a-50 and 3.25a-60) do not induce evident further modifications on the fibers. It is worth noting that no modification of the average fiber diameter was observed, irrespective of the length of the oxidation treatment.

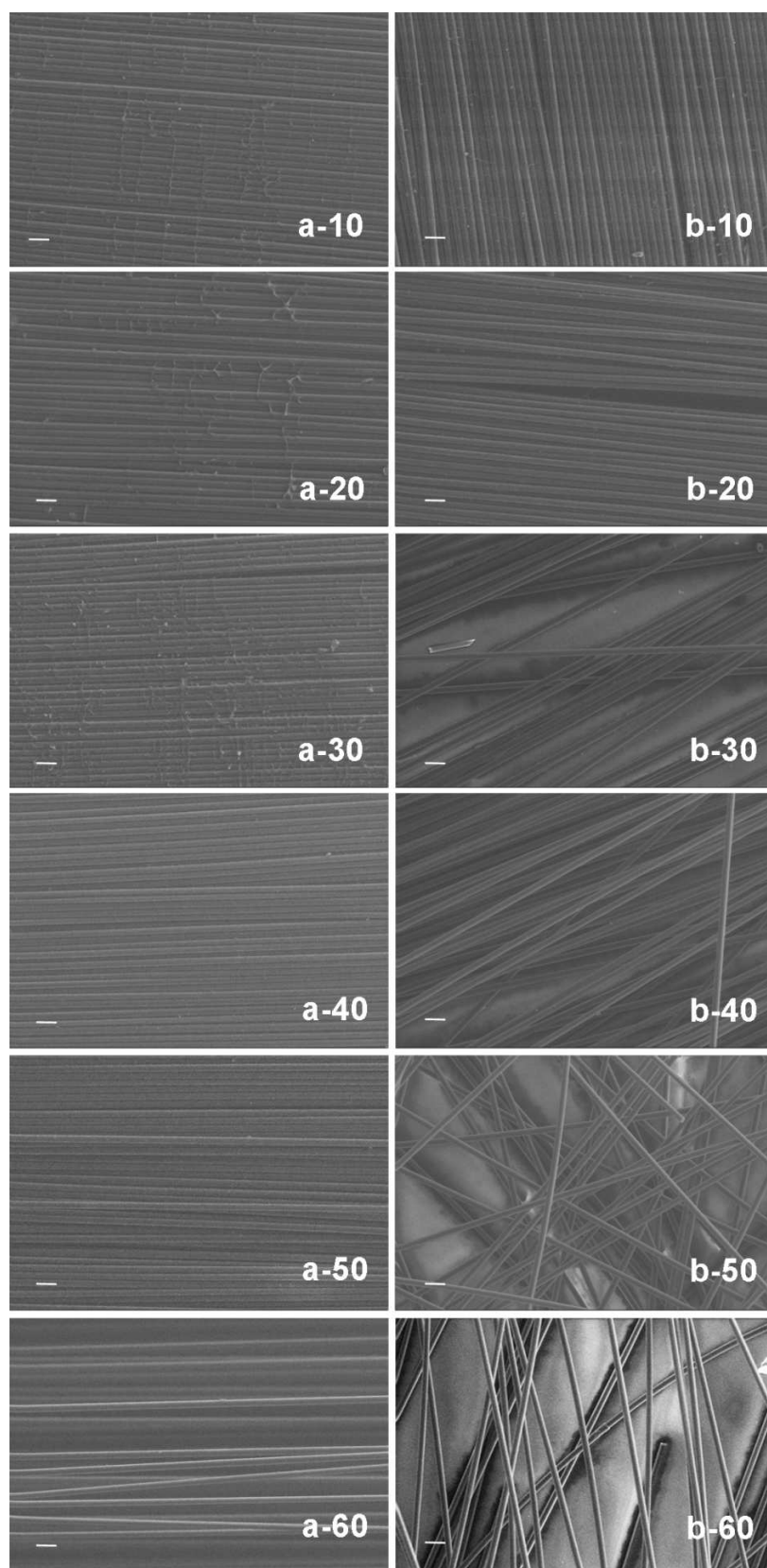


Figure 3.25 - SEM micrographs of cured scraps pyrolyzed and oxidized at 500°C (a) and pyrolyzed and oxidized at 600°C (b) for different time (10, 20, 30, 40, 50 and 60 minutes) [66]. Reproduced by permission of Wiley.

The solid residue coming from pyrolytic batch carried out at 600°C contains fibers definitely less covered by non-degraded resin. Thus, the oxidative process at 600°C only takes 10 minutes to provide fibers connected by few thin resin bridges while 20 minutes are sufficient to clear them from any residue. Longer oxidation times do not induce visible surface damage of the fibers, though a decrease of their average diameter is observed (from 6.9 to 6.5µm) when the oxidation time increases from 20 to 60 minutes.

In order to better understand the characteristics of the carbonaceous layer observed in the SEM micrographs, all the CFs oxidized at different temperatures and for different timespan, together with the pristine ones, were analyzed by Raman spectroscopy coupled with optical microscope to guide the Raman probe. All the Raman spectra, focused in the 1000-2000 cm^{-1} spectral range, where all samples display significant signals, are shown in Figure 3.26.

These signals are well known in the literature [69] for carbonaceous materials, both amorphous and graphitic. In particular, the main absorption observed in the spectra around 1560 and 1360 cm^{-1} , are usually attributed to the so-called G and D peaks respectively. In particular, the G-peak is ascribed to the bond stretching of all pairs of sp^2 atoms in both rings and chains, while the D-peak is due to the defect induced on the sp^2 structure [69]. In principle, evaluation of the intensities of these two signals can be directly correlated to the fraction of graphitic and amorphous carbon. However, it is quite difficult to provide evidence of surface quality modification when virgin Carbon Fibers has low graphitization degree, as in this case. Nevertheless the sharpness of these peaks can be correlated with the lack of organic residues (amorphous carbonaceous layer) [70] and it is taken as a significant hint to guarantee that the oxidation process provides a surface free from any residual resin, as observed qualitatively by SEM micrographs [25]. Indeed, Raman spectrum of the fibers obtained directly from pyrolysis presents broad and poorly defined D- and G-peaks, owing to the presence of organic residues on the fiber surface, as already observed in SEM micrographs (Figure 3.23-f and 3.23-g). The same broad Raman absorptions are observed in the fibers oxidized at 500°C up to 30 minutes treatment, while, when CFs are treated at 600°C, they can be detected only for the sample treated for 10 minutes. Increasing the oxidation time by 10 mins in both cases, the D- and G-peaks results significantly narrower and sharper, thus suggesting an almost complete removal of residual resin. These results strongly agree and confirm observations based on the SEM analysis.

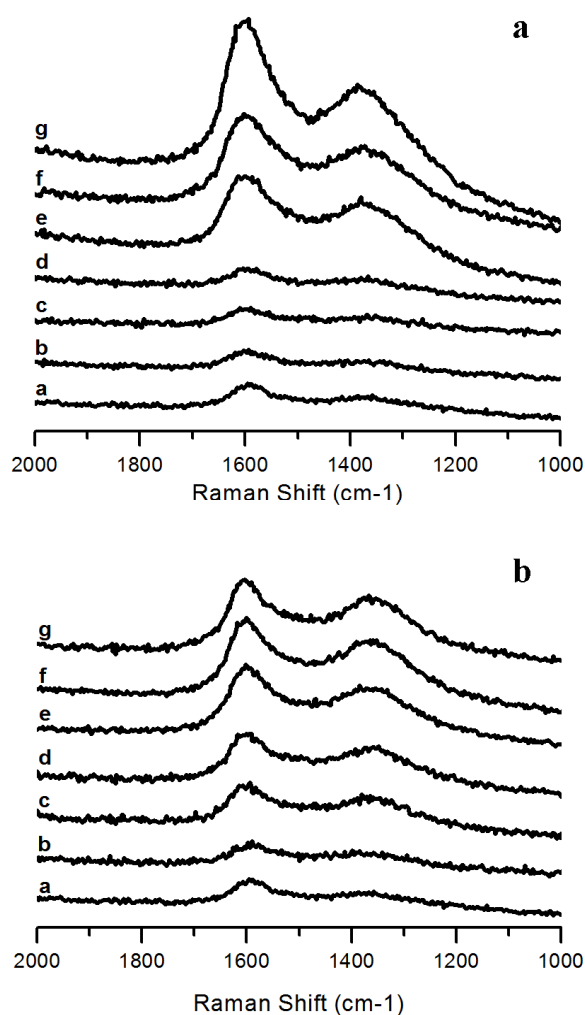


Figure 3.26 - Raman spectra of cured scraps pyrolyzed at 500°C (A-a) and 600°C (B-a). Raman spectra of cured scraps pyrolyzed and oxidized at 500°C (A) and pyrolyzed and oxidized at 600°C (B) for 10 (b), 20 (c), 30 (d), 40 (e), 50 (f), and 60 (g) minutes [66]. Reproduced by permission of Wiley.

3.3.6. Reclaiming fibers

Carbon fibers obtained as pyrolytic residue show the same arrangement of the pristine materials. This means that, being pyrolysis a recovery treatment applied to different kind of waste, no assumptions can be made on the actual aspect of the obtained fibers, being them plain woven, twill or unidirectionally aligned. Though plenty of literature is devoted to the characterization of the single fiber mechanical properties [68, 71] after pyrolysis, it is very difficult to foresee for such materials a re-use in the very same applications as the pristine ones, at least because of the form factor hampering a wide number of applications. Hence, in order to assess the possibility of re-using the long recycled CFs obtained at different operational

conditions, in the present work the fibers have been manually chopped to a length ranging from 25 to 50 mm and used as reinforcing agents for a commercial epoxy resin system, obtaining Chopped Carbon Fibers Reinforced Composites (Re-CCFRCs).

Fibers to be used in Re-CCFRC are easily recovered by dimensionally inhomogeneous pyrolytic residues recovered from scraps of variable shape and fiber type. Though in general CCFRCs cannot reach the outstanding performances of the long fibers ones, they are used for a wide number of applications such as internal panels for automotive, lightweight sports equipment and more generally where the lightness is a premium property but the performance is not. Up to now, such composites are produced using the very same kind of high value fibers used for far more highly demanding applications. Thus, the possibility of using some recycled fibers, whose mechanical properties appear to be 65-95% of the initial values [71] might be economically promising and might also help widening the fields of use of such chopped carbon fibers composites.

Hence, recycled fibers have been chopped down to a suitable length (Figure 3.27a) and impregnated with a two-components epoxy resin formulation (feed: CCF/resin 1/1 ratio). The impregnation process has been carried out manually (Figure 3.27b) and the mixture poured in a steel mold (200x150 mm) (Figure 3.27c) that has been placed in a hot plate press (110 °C 40 min. 45 bar). Since this work is intended as a preliminary investigation of the possibility of producing CCFRC with fibers from pyrolysis (Re-CCFRC), just two representative fiber samples have been selected for composites production. In particular composites have been produced with fibers obtained from pyrolysis of cured scraps carried out at 500°C, and further oxidized at 500°C for 60 mins (Re500-P500-60), and at 600°C, and further oxidized at 600°C for 30 mins (Re600-P600-30). These two cases represent the most extreme treatment conditions that are able to lead to clean and flexible fibers apparently similar to the pristine ones. For the sake of comparison, additional Re-CCFRCs have been produced: two with fiber obtained from the pyrolysis batch on cured scraps carried at 500°C (Re500) and at 600°C (Re-600) respectively, without any further treatment, and a third obtained using pristine dry fibers (VF). Thus have been obtained composites which appear as flat panels with rough borders (Figure 3.27d) and which have been cut in bars suitable for further mechanical tests. With the aim to assess the carbon fibers fraction in each composites, all the samples have been analyzed by TGA in oxidizing atmosphere. Each TGA thermograms, carried out up to 600°C in order to not exceed the pyrolysis/oxidation temperatures applied, displays a single stepwise degradation process attributed to thermo-oxidation of the resin component [24] that, irrespective of the fiber used, begins around 320°C. Consequently, the solid residue at 600°C is attributed to the carbon

fibers fraction and is used for estimating the actual composition of the samples, as reported in Table 3.20.

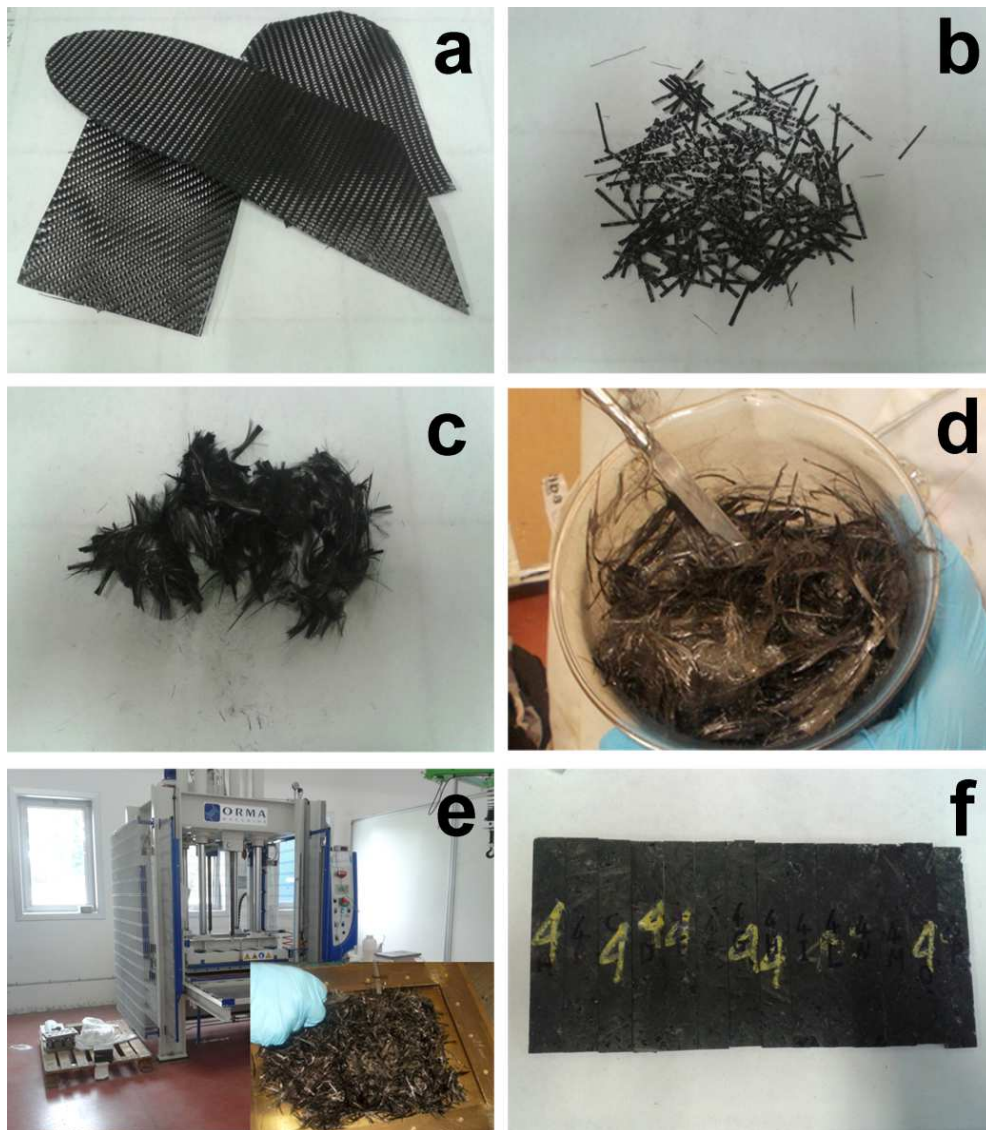


Figure 3.27 - Process steps for the Re-CCFRC production: Carbon Fibers recovered from pyrolysis batches (a) have been cut down to 25mm length (b) and then oxidized to remove the carbonaceous layer. The obtained CFs (c) have been mixed with two-component epoxy resin mixture (d) and cured in a hot press mold (e) to obtain flat panels which have been cut into 100x15 mm stripes (f) [66]. Reproduced by permission of Wiley.

Worth noting is that all the samples composition, but in the case of Re500, well compares with the feeding, meaning that the impregnation process succeeded in homogeneously mixing the two components. In the case of Re500, fibers are not further oxidized and they still present resin residues that make them stiff and compact, even after the chopping: this is probably the reason because in just this case the mixing between the fluid

epoxy formulation and the fibers did not perfectly succeeded, resulting in areas with different fiber to resin relative composition. The Re600 composite is not as affected as the Re500 from the lack of further treatment, since the higher pyrolysis batch conditions are able to provide more flexible fibers, even without additional treatments.

Table 3.20 - Thermo-mechanical properties of Re-CFRC [66].

Sample	Solid residue^a (wt%)	Apparent density^b (g/cm³)	Young's Modulus E (GPa)	Stress at break (MMPa)	Elongation at break (%)
VF	44	1.2	1.9±0.3	114±12	9.5±2.3
P500	63	0.9	1.3±0.3	53±8	3.9±1.2
P600	56	1.0	1.3±0.2	38±6	3.9±0.6
Re500-P500x60	52	1.2	1.8±0.3	93±28	8.7±2.9
Re500-P600x30	49	1.2	1.8±0.3	71±10	5.1±0.4

^aCalculated by TGA at the end of a 10°C/min heating scan from RT to 600°C.

^bDetermined as the ratio between weight and volume of the single bars used for mechanical tests.

Once they are cut, all panels nevertheless show some voids and defects, possibly due to heterogeneities during the mixing. Hence, in order to assess the quality of the Re-CCFRCs sample bars that are intended for mechanical tests, each bar has been measured and weighted and an average apparent density has been calculated for each sample. As shown in Table 5, all the obtained composites panels are characterized by an average density lower than that expected for an epoxy resin carbon fiber composite (around 1.5/1.6 g/cm³) [72]. This behavior suggests that a no good compaction has been reached probably because in the hot press the composite has not enough time to compact before the resin cross linked. It is worth noting that the lower densities are shown by Re500 and Re600 (0.9 and 1.0 g/cm³ respectively) which have been obtained from un-oxidized fibers that, as already discussed, are more rigid. Furthermore, the lower the pyrolysis temperature the lower the density.

Mechanical tests have been carried out in tensile mode in order to provide comparative properties of the composites obtained with pristine and recycled fibers. As a guideline, have been chosen to analyze 10 samples for each formulation, whose density is the closest to the average value, in order to discard possible macroscopic voids or defects that might affect the samples properties. As reported in Table 3.20, properties of VF are similar to those observed with the two composites obtained from fibers recycled and thermally oxidized in air, namely Re500-P500-60, and Re600-P600-30. The Young's Modulus (Table 3.20) of these materials is well comparable and accounts for the possibility of using these recycled fibers as raw materials

for composite production. On the other hand, ultimate properties at break slightly differ, diminishing when pyrolytic and oxidized fibers are used. Such a behavior can be ascribed to a poorer matrix-fiber adhesion with respect to pristine carbon fibers, that, however, are coated with sizing. Moreover, though no broken fibers have been observed after pyrolysis and oxidation treatment, high temperature treatment might nonetheless affect the intrinsic mechanical properties of the fibers as reported by Meredith [71]. Furthermore, should be considered that the results can be affected also by some defects due to the production method applied for producing the composites. Hence SEM micrographs were taken at the fracture surface of the VF, Re500, and Re500-P500-60 samples subjected to stress/strain tests (Figure 3.28) in order to assess the aspect of the fibers once the sample was pulled apart. The images show that both the VF and Re500-P500-60 (Figure 3.28a and Figure 3.28c) samples display signs of matrix/fiber debonding that left grooves in the resin where fibers detached. Furthermore the fibers aspect is similar for the two samples resembling their appearance before being included in the composite (see Figure 3.25), thus not accounting for any evident fiber damage caused either by the pyrolytic and oxidative treatment or the mechanical test. In the case of Re500 sample, though, at the fracture surface fibers are well aligned (Figure 3.28b), as in a bundle, and they appear clean and well dispersed, with some hint of the carbonaceous coating, well resembling those reported previously in the micrographs from Figure 3.23. A very minor fraction of the resin matrix appears in the picture, as though it was hardly infiltrated in the fiber bundle during the impregnation step. This result well compares with the previous observation that showed Re500 as the only component with a different resin/fiber fraction with respect to the feeding. Moreover the two Re-CCFRCs obtained from no oxidized CFs (Re500 and Re600), show a definitively lower Young's Modulus. Since they both are characterized by lower density, the reason of such a behavior can be thus attributed to a lower compaction of the uncured mixture in the hot press and to the poor flexibility of the raw fibers, that without any further treatment are too stiff to be used. This stiffness is a symptom of no-degraded resin residues and carbonaceous layers covering the fiber bundles and hampering the fluid epoxy resins precursors from well wetting the single fibers, as demonstrated by Figure 9-b. Hence, in order for the pyrolytic fibers to be positively re-used, evidence is given that oxidation treatments are necessary.

Finally, it is worth to note that the choice of oxidizing the fibers at the same temperature used for pyrolysis can foresee the application of an *in line* thermal treatment carried out directly on the hot solid residue at the end of the pyrolysis process, when up-scaling to a continuous plant.

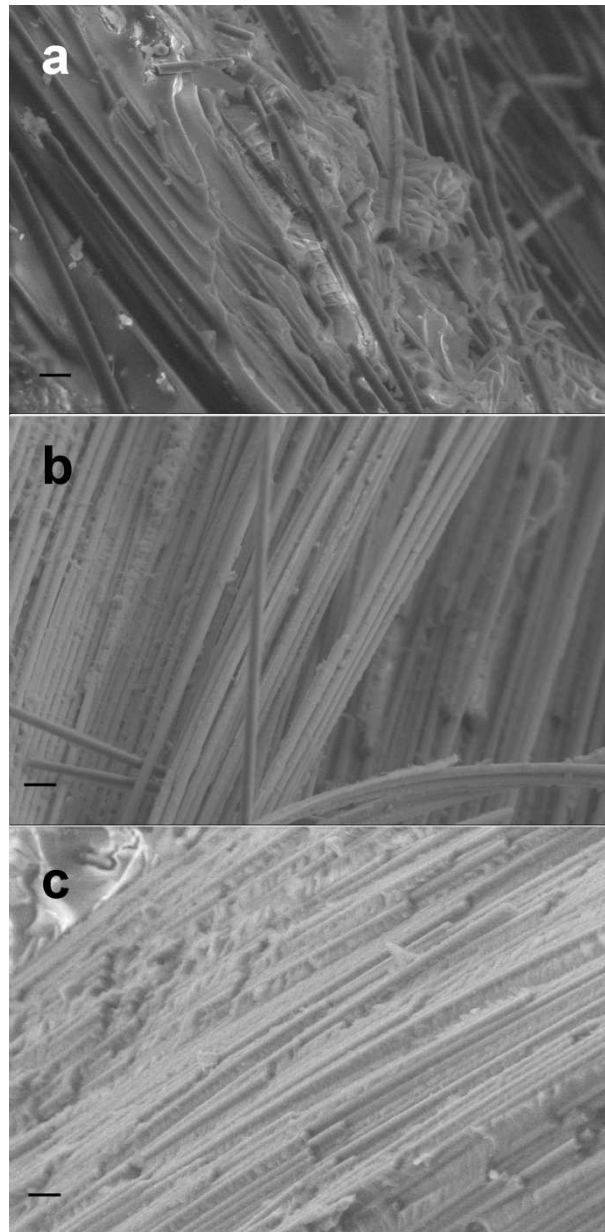


Figure 3.28 - SEM micrographs of the fracture surfaces taken after mechanical test for VF (a) Re500 (b), and Re500-P500-60 (c) composites samples. Scale bar: 20 μ m [66]. Reproduced by permission of Wiley.

3.3.7. Conclusions

This work provides some preliminary evidence on the possibility of applying a coupled pyrolysis/oxidative process to CFRCs wastes in order to recover carbon fibers to be re-used for new composites production.

Though the pyrolysis tests were carried out in a demonstrative pilot plant non-optimized in terms of energy balance, the gaseous and liquid by-products can sustain about 75% of the process energy requirement. It is hence possible to foresee that, upon a convenient optimization

of energy issues during scale up, the process might reach a complete energetic self-sustainability.

The CFs recovered after pyrolysis appear covered by a layer of amorphous carbonaceous derivatives and the resin results non completely degraded. These recovered CFs are stiff and not easily wetted by the resin precursor, resulting in a poorer composites overall performance.

With this study have been demonstrated that by a further thermal treatment in air at high temperature between 500-600°C (oxidation) it is possible to obtain clean CFs which can be re-used to provide Chopped Carbon Fiber Reinforced Composites (Re-CCFRCs) with performances comparable to those obtained with pristine fibers: at 500°C the time of air exposure should be 40 minutes or more; at 600°C the contact time with the oxidative atmosphere should be about 20 minutes in order to avoid the risk of damaging the fibers by surface oxidation.

Furthermore, by running the pyrolysis and the oxidation processes at the same temperature (e.g. 500 or 600°C), it is possible to plan an *in line* thermal treatment carried out directly on the hot solid residue at the end of the pyrolysis process, when up-scaling to a continuous plant. The present results thus pave the way to the application of recovered carbon fibers in the production of chopped fibers composites.

3.4. Pyrolysis of fiberglass

This study is part of a project aimed at the disposal of non-shredded fiberglass wastes in a non-dangerous pyrolysis pilot plant, with recovery of chemical feedstocks from the polyester resin and the simultaneous fibers separation. A subsequent oxidation step to remove the carbonaceous residue coated on the fibers is evaluated in order to obtain clean and reusable glass fibers.

The glass fiber-reinforced polyester composite samples (GFRPs) are cutout scraps coming from manufacturing process of polyester laminates with glass fiber MAT. The samples have been received in the form of sheet rolls with thickness 2.5 mm, width about 250 mm and a length up to 3m (Figure 3.29a). The samples are composed of an isotropic glass fiber mat reinforcement with a polyester matrix covered with a protective low density polyethylene (LDPE) thin film on one side (Figure 3.29b).

All samples have been pyrolyzed without any further treatment, meaning that no shredding nor crushing have been applied.



Figure 3.29 - Typical glass fibers reinforced polyester resin laminate scraps (a) and a focus on LDPE protective film (b).

3.4.1. Characterization of feed material

In order to set up conditions for pyrolysis experiments, a preliminary thermogravimetric investigation (TGA) of GFRC sheet without LDPE protective film has been carried out in dynamic mode and inert atmosphere. The thermogravimetric curve reported in Figure 3.30 shows a degradation starting at around 300°C, while its T_{onset} is determined around 390°C: the degradation process ends leading a constant weight residue (32.4wt%) after 80 minutes at 550°C. These preliminary TGA experiments do not take into account the presence of the LDPE

coating. However, since literature [67] reports that the presence of polyethylene leads to the formation of waxes which could condense at low process temperature, pyrolytic tests at temperature below 500°C have not been performed in order to avoid pipeline obstruction. Hence, given TGA results, the range 500-600°C has been selected for further pyrolysis experiments in the pilot plant: different tests have been performed every 50°C.

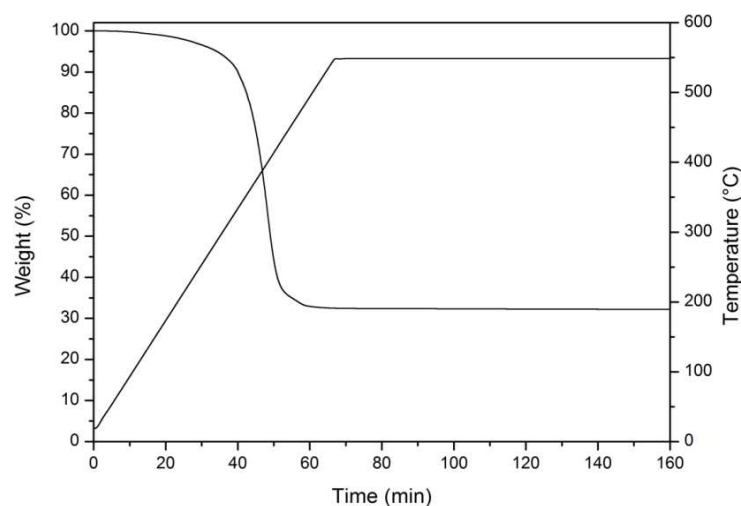


Figure 3.30 - TGA thermogram of GFRPs polyester laminate without LDPE protective film.

Once suitable temperature ranges have been identified, pyrolysis experiments have been performed in a batch pilot plant from Curti S.p.A [54], where each raw material load is about 20 kg. The pyrolytic process on GFRPs has led to three main products streams, i.e. a gas phase, an oil fraction and a solid residue. Their relative ratios depend on the applied reaction conditions (such as temperature and residence time). After determining the optimal residence time for the materials to be 2.5 hours, of which the effective pyrolysis step takes only about 20-30 minutes to complete, different temperatures have been tested.

Figure 3.31 shows the yields of the obtained solid residue, oil and gas (the latter calculated by difference) upon pyrolysis as a function of the reaction temperature. The figure shows that only limited differences appear in product distribution at 500 and 550°C. The total amount of solid residue, composed of glass fibers covered of a carbonaceous layer similar to coke in appearance, tends to a slight decrease from 44.3 to 43.8 wt%.

When the process temperature increases up to 600°C, the solid residue and the oil fraction decrease from 43.8 to 38.7 wt% and from 19.2 to 16.9 wt% respectively. By contrast, the non-condensable fraction, calculated by difference, tends to increase from 37.0 to 44.4 wt%. Thus, in highest temperature experiment, the oil/syngas weight ratio decreases from 0.54

to 0.38. A similar trend was found by Torres et al. [73] pyrolyzing GFRPs although the oil/syngas ratio was greater than one. The decrease of the oil/syngas weight ratio with the increase of temperature are reported also for other polymeric matrix composite materials such as tires [39, 46]. This phenomenon can be explained taking account further cracking of evolved volatile matter at elevated temperatures [39]. The increase in the syngas fraction can also provide explanation for the lower solid residue observed at 600°C. Indeed, the formation of carbonaceous residue is due to secondary repolymerisation reactions among the polymeric derived pyrolytic products. Upon raising the process temperature, the decomposition of the polyester resin is boosted, thus generating more non condensable products and decreasing the percentage of the organic solid residue that cannot repolymerize to form the carbonaceous coating onto the fibers.

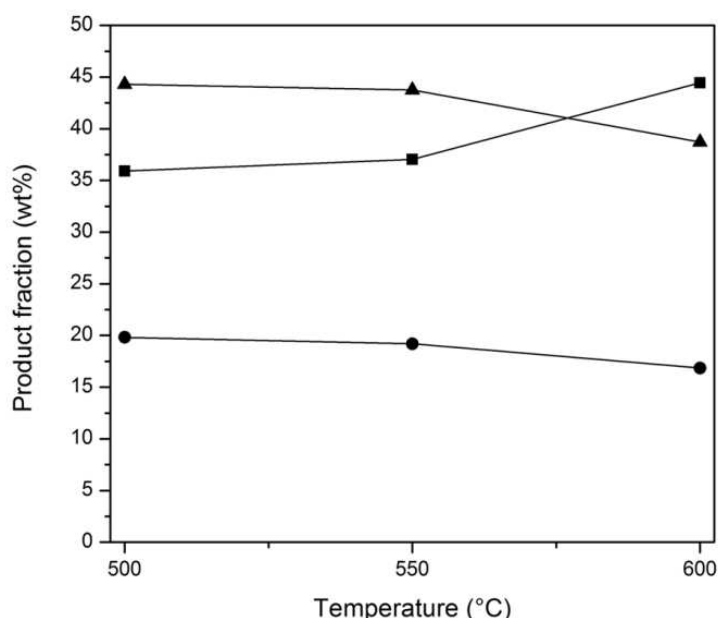


Figure 3.31. Products distribution at different pyrolysis temperature. (▲) Solid residue; (■) Syngas; (●) Oil phase.

3.4.2. Oil characterization

The GFRPs pyrolysis condensable fraction within the cooling system is a complex mixture of organic compounds whose relative concentrations are primarily influenced by the process temperature [74]. GC-MS analysis has revealed the presence of benzene and its alkyl derivatives (such as toluene, ethylbenzene, cymene, propylbenzene), styrene and α -methylstyrene, benzaldehyde and acetophenone, indene and its derivatives, naphthalene and methylnaphthalenes. Among the detected compounds, benzene, toluene, ethylbenzene and styrene have high market values as a source of light aromatics, hence their quantification has

Results and discussion

been carried out for each batch and the results are reported in Table 3.21. The maximum concentration of the compounds of interest is registered in the oil produced at 550°C and corresponds to 84.3 g/l.

Table 3.21 - Benzene, toluene, ethylbenzene and styrene content (g/l) in oils obtained at different temperatures.

Oil components	Process temperature (°C)		
	500	550	600
Benzene	3.4	9.5	6.8
Toluene	15.0	31.1	27.3
Ethylbenzene	16.7	30.0	21.5
Styrene	7.9	13.7	13.6

In order to estimate their potential commercial value, oils produced via pyrolysis at different temperatures have been analyzed by XRF which allows to disclose the presence of possible contamination. The results are reported in Table 3.22 together with their density and viscosity.

Table 3.22 - XRF analysis (wt%), density and viscosity of the oils obtained by pyrolysis at different temperatures.

Oil contaminants	Process temperature (°C)		
	500	550	600
Cl	-	0.07	0,06
Na	0.16	-	0,33
Si	0.03	0.01	0,02
Al	-	-	0,02
S	0.05	0.01	0,02
Characteristics			
Density (g/cm ³)	1.013	1.011	1.014
Viscosity (cSt)	27.1	16.2	20.1

All the oils result composed mainly of carbon, hydrogen, nitrogen, and oxygen and just a slight amount of sodium (0.16-0.33 wt%) and sulphur (0.01-0.05 wt%) have been found in all the analysed samples. Silicon and chlorine are always well below 0.1%wt. Hence, the low content of sulfur and halogens, and the total absence of heavy metals make the obtained pyrolysis oils suitable as fuel without the need for any further purification process.

The density of the obtained oils results constant with the process temperature while the viscosity values vary in the range 16.2-27.1 cSt.

3.4.3. Syngas characterization

The volatile mixture evolving during the experiment has been continuously monitored online through a micro-GC during the pyrolysis tests in order to correlate the syngas composition with the applied process conditions. The detected gases are carbon oxides (CO and CO₂), hydrogen, methane, ethane, and ethylene. The sum of propane and propylene is named C₃, while the sum of 1-butene, n-butane, 1,3-butadiene, iso-butylene is named C₄. “Others” is the sum of the other indeterminate incondensable species, mainly composed of C₄₊.

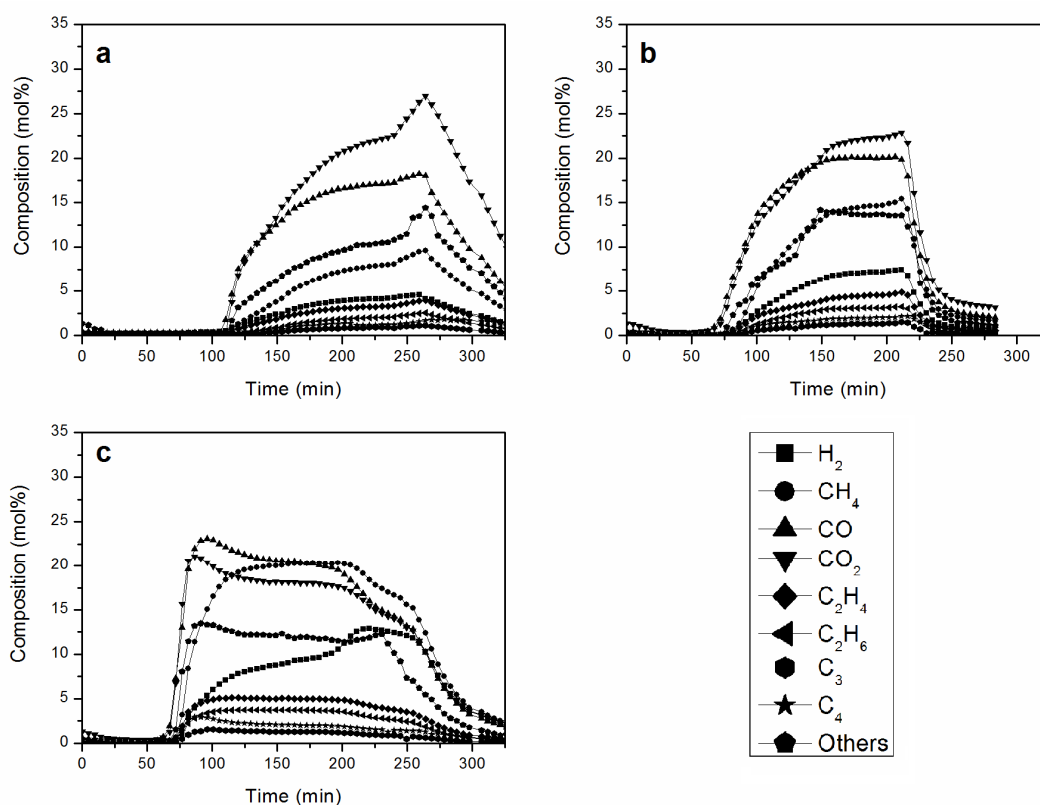


Figure 3.32 - Composition of the syngas during the run at (a) 500°C, (b) 550°C and (c) 600°C with fiberglass.

Table 3.23 shows the average composition of the syngas produced at different pyrolysis conditions. In additions, Gross Calorific Value (GCV) of each mixture is presented (Table 3.24).

At 500°C the main evolved compound is CO₂ (32.6 vol%) followed by CO (24.2 vol%) primarily generated upon the breakdown of oxygen-rich moieties which are abundant in the polyester resin formulation. In this experimental condition there are considerable fractions of methane (10.6 vol%) and hydrogen (5.8 vol%). With the increase of the process temperature the syngas is enriched in the most volatile components such as H₂ and CH₄ while a significant

reduction in oxides content is registered, mainly due to a decrease of the carbon dioxide component from 32.6 to 20.4 vol%. [74], did not detect the presence of hydrogen in the gaseous fraction obtained by pyrolysis of similar GFR polyester resins. In their work, the Authors obtain high concentrations of carbon oxides and report that the C₁-C₄ species reach a maximum of 9.4 vol% at 700°C. Lopez et al. [28] at 550°C found concentrations of CO (21.26 vol%) and CO₂ (37.51 vol%), comparable with those determinate in this study, though the hydrogen fraction in their work was only 2.3 vol%.

Table 3.24. Chemical composition and GCV of the gas produced by pyrolysis of GFRPs scraps (vol%) at different process temperature.

Syngas components	Process temperature (°C)		
	500	550	600
H ₂	5.8	7.5	11.5
CH ₄	10.6	15.4	20.7
CO	24.2	24.0	21.8
CO ₂	32.6	26.0	20.4
C ₂ H ₄	4.8	5.0	5.2
C ₂ H ₆	2.8	3.3	3.7
C ₃	1.4	1.4	1.3
C ₄	2.6	2.7	2.5
Others	15.2	14.7	12.9
GCV (MJ/Nm ³)	31.1	33.3	34.1
GCV (MJ/kg)	24.9	27.5	30.0

The calorific value of a gas is function of the chemical composition and relative amounts of its chemical species. By means of the compositions obtained by μ -GC analysis and utilizing the standard method UNI 7839, it has been possible to evaluate the Gross Calorific Value (GCV) of the syngases (Table 3.24) which increases from 31.1 to 34.1 MJ/Nm³ by increasing pyrolysis temperatures. This is due to the mentioned decrease of CO₂, which of course has non calorific potential at all. These values are higher than those reported by Torres et al. [65] (14.1-16.4 MJ/Nm³) and similar, although higher, with respect to the data obtained from Lopez et al. [28] at 550°C.

3.4.4. Solid residue and recovered glass fibers characterization

Figure 3.33a shows the black solid residue obtained by pyrolysis which looks dimensionally analogous to the feeding fiberglass reinforced composite scraps (Figure 3.29). This residue, whose amount decreases from 44.3 to 38.7 wt% increasing the process temperature from 500 to 600°C, is composed of glass fibers mats where the fibers are randomly arranged and kept together by a thin cohesive carbonaceous layer, thus providing the overall black colouring.



Figure 3.33 - Solid residue recovered from pyrolysis batches (a, b) and clean recovered glass fibers after oxidation to remove the carbonaceous layer (c, d).

In Figure 3.34, SEM micrographs of solid residues obtained in the different pyrolysis conditions are reported. All the fibers show an uneven surface, due to char deposits, as previously stated [74].

In the pyrolyzed samples, the average fiber diameter decreases from 15.0 to 13.5 μm when the process temperature increases from 500 to 600°C (Table 3.25).

In order to quantify the extent of char fraction and the thickness of the carbonaceous layer, the carbon residue has been completely removed through an oxidizing treatment on the

solid residue obtained for each pyrolysis temperature, as demonstrated by the picture reported in Figure 3.33c.

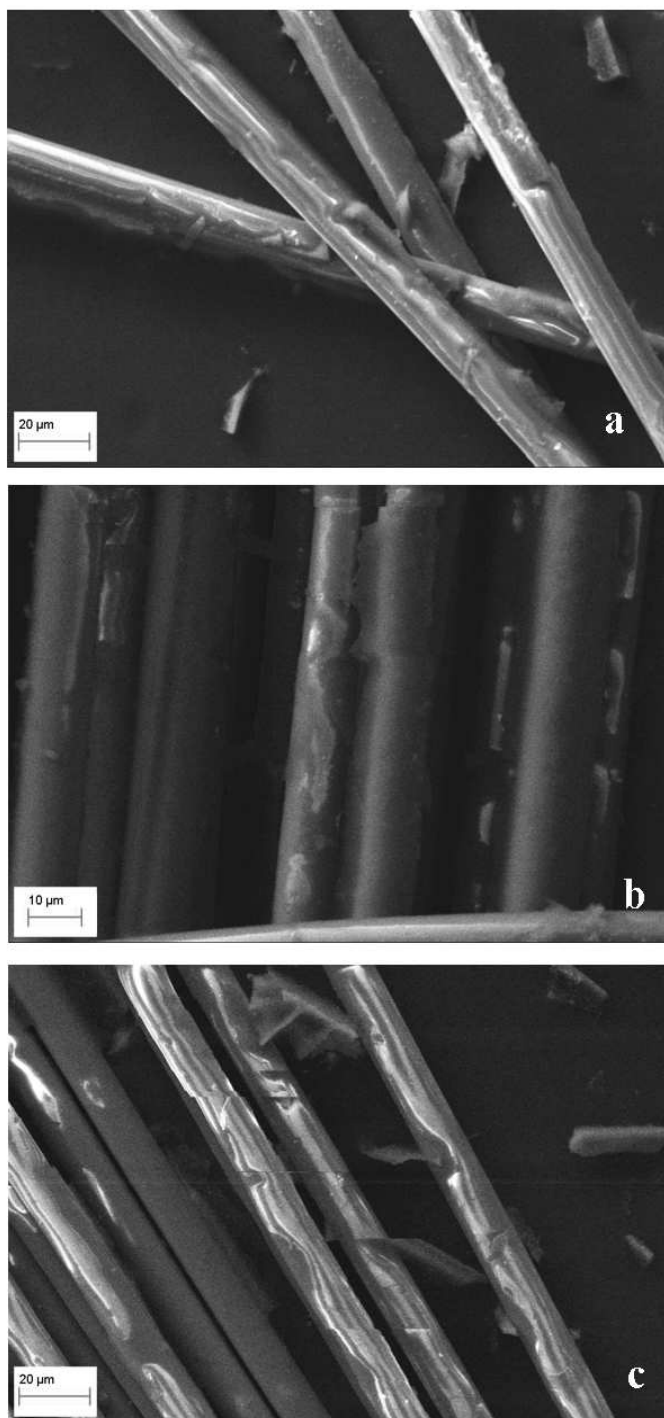


Figure 3.34. SEM micrographs of solid residue obtained at different process temperature: 500, 550 and 600°C.

Table 3.25 - Sizing of the carbon deposits on the glass fibers obtained at different pyrolytic process temperature.

Pyrolysis process temperature (°C)	Average diameter of the glass fiber (μm)		Thickness of carbon deposits (μm)
	After pyrolysis process	After oxidation	
500	15.0	12.5	1.25
550	14.4	12.5	0.95
600	13.5	12.5	0.50

The weight loss during the oxidizing treatment are in the range between 21.3 and 16.8 wt% and decreases with the increase of pyrolysis process temperature. The inorganic components in the pyrolysis-oxidized residues, calculated according to the equations proposed by Torres et al. [73], correspond to an average 34 wt%. The most notable observation upon the oxidation treatment is that fibers become perfectly white, as reported in Figures 3.33c and 3.33d.

SEM images of the solid residue obtained from the pyrolysis of GFRPs at 550°C, before and after the oxidation treatment at 600°C for 60 minutes, are shown in Figure 3.35. These micrographs display clearly that, after the oxidation treatment, the glass fibers appears smooth and flawless, and the carbonaceous coating has been completely removed. Moreover the average diameter of the treated glass fibers is now reduced to 12.5 μm, this value being taken as the diameter of the virgin uncoated fibers. So, the thickness of carbon deposit on the fibers is estimated to be about 0.95 μm. The same procedure has been applied to the glass fibers obtained by pyrolysis at other temperatures (Table 3.25) and shows a decrease of the calculated thickness of the carbonaceous layer from 1.25 to 0.50 μm when the pyrolysis process temperature increases from 500 to 600°C. In all the analyzed cases (Table 3.25) after the oxidation treatment the fibers reach a constant diameter of 12.5μm, thus confirming that this can be safely taken as the reference thickness of the average naked glass fiber.

The disappearance of the carbon residue deposited on glass fibers, as a function of oxidation temperature and time residence, has also been followed by Raman spectroscopy coupled with optical microscope to guide the Raman probe.

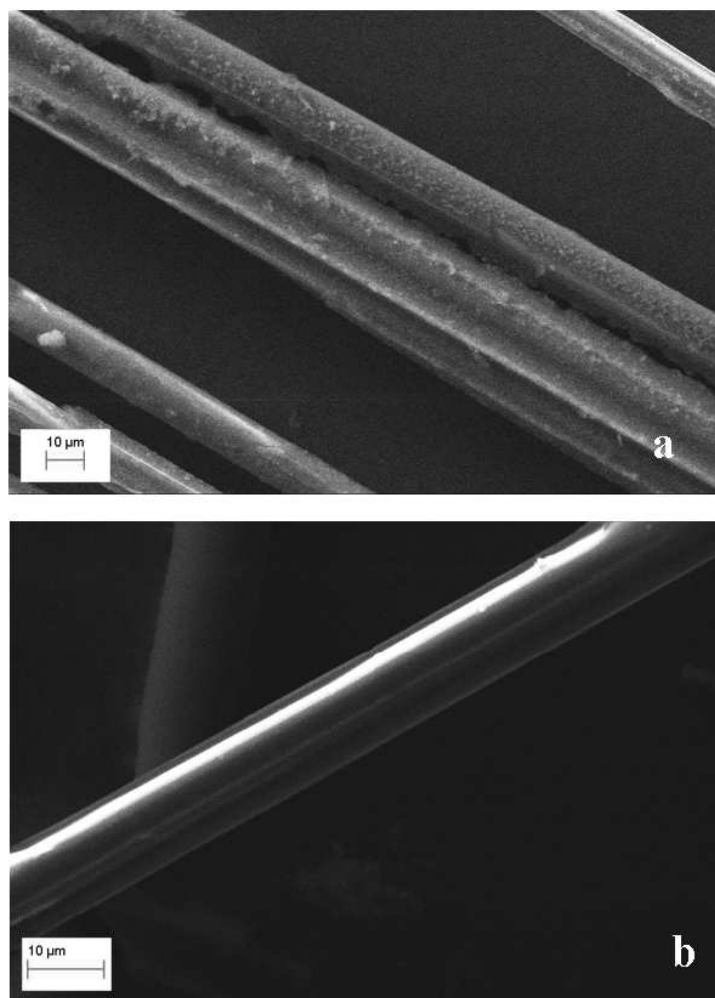


Figure 3.35 - SEM micrographs of recovery solid residue pyrolysed at 550°C (a) and subsequently oxidized at 600°C (b) for 60 minutes.

In particular, have been analyzed the solid residue obtained by pyrolysis at 500°C and subjected to a subsequent oxidation treatment at 500°C for 10, 20, 30, 40, 50 and 60 mins. The Raman spectrum of the solid residue obtained after pyrolytic process at 500°C is shown in Figure 8 and exhibit two evident broad peaks at 1560 and 1360 cm^{-1} that are well renowned absorption for carbonaceous materials as the so-called G and D peaks respectively [69]. In particular, the G-peak is ascribed to the bond stretching of all pairs of sp^2 atoms in both carbon rings and chains, while the D-peak is due to the defect induced on the sp^2 structure [69].

The presence and intensity of these peaks can be correlated with the presence or lack of organic residues (amorphous carbonaceous layer) [70] and it is taken as a significant hint to guarantee that the oxidation process provides a surface free from any residual resin, as observed qualitatively by naked eye and SEM micrographs (Figure 3.33 and Figure 3.35, respectively).

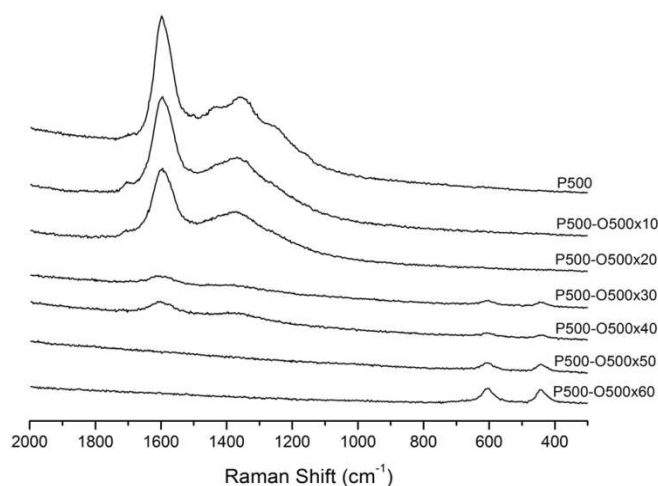


Figure 3.36 - Raman spectra of solid residue (P500) obtained by pyrolysis at 500°C and for the same residue oxidized at 500°C (P500-O500x) for 10, 20, 30, 40, 50 and 60 minutes.

The same broad Raman absorptions are observed in the fibers oxidized at 500°C up to 40 minutes treatment (Figure 3.36). Increasing the oxidation time by 10 mins, the D- and G-peaks are absent, thus suggesting an almost complete removal of residual resin. The complete removal of the carbonaceous residue results in the appearance of three new peaks at lower Raman shift, that can be ascribed to the glass fibers (Figure 3.36).

To evaluate the effect of higher oxidation temperatures on glass fibers, the same solid residue (obtained by pyrolysis at 500°C) has been subjected to oxidation at 600°C for 10, 20, 30, 40, 50 and 60 minutes and the evolution of the carbonaceous residue has been followed again by Raman spectroscopy. The obtained Raman spectra are presented in Figure 3.37.

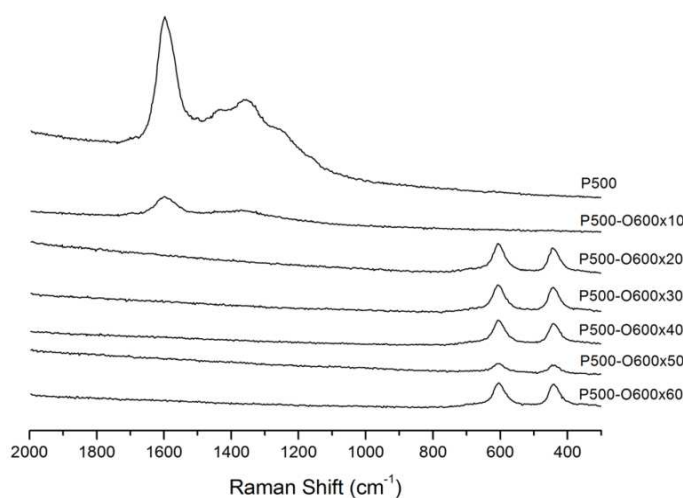


Figure 3.37 - Raman spectra of solid residue obtained by pyrolysis at 500°C (P500) and for the same residue oxidized at 600°C (P500-O600x) for 10, 20, 30, 40, 50 and 60 minutes.

At 600°C, only 20 minutes are needed to completely remove the carbonaceous residue from the surface of the fibers, as evidenced by the disappearance of the characteristic peaks at 1560 and 1360 cm⁻¹. By increasing the residence times, no structural changes of the glass fibers have been highlighted through the Raman spectra.

When applying the minimum oxidation time residence necessary for the complete removal of the carbonaceous residue (50 minutes at 500°C and 20 minutes at 600°C) to solid residues obtained upon pyrolysis at 550 and 600°C, Raman spectroscopy (Figure 3.38) confirms once again the complete removal of the carbonaceous coating without inducing detectable structural changes.

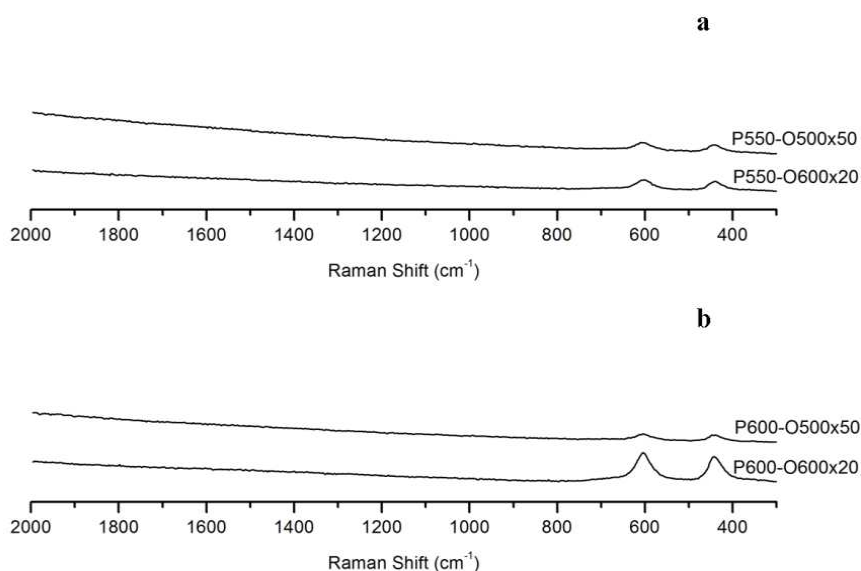


Figure 3.38 - Raman spectra of glass fibers obtained by oxidation treatment at 500°C for 50 minutes (O500x50) and 600°C for 20 minutes (O600x20) on both pyrolysis solid residues obtained at (a) 550 (P550-) and (b) 600°C (P600-).

Longer oxidation times do not induce visible surface damage of the glass fibers and their average diameter stays constant at 12.5 μm when the oxidation time increases from 10 to 60 minutes also at higher temperatures.

These data confirm previous findings observed on pyrolyzed carbon fibers from carbon fiber reinforced composites pyrolysis, that show similar conditions for the complete removal of the outer carbon layers [66]. Furthermore, by running the pyrolysis and the oxidation processes at the same temperature (e.g. 500 or 600°C), it is possible to plan an *in line* thermal treatment carried out directly on the hot solid residue at the end of the pyrolysis process, when up-scaling to an industrial plant.

3.4.5. Conclusions

Pyrolysis resulted a highly suitable method for recovering glass fibers from GFRPs scraps in an almost self-sustained process. The proposed process yielded an oil ($\approx 20\text{wt}\%$), a gas ($\approx 40\text{ wt}\%$) and a solid residue ($\approx 40\text{wt}\%$). The syngas appears significantly rich of H_2 and CH_4 . Moreover, have been demonstrated that, by a further oxidation treatment at temperature between $500\text{-}600^\circ\text{C}$, it is possible to obtain clean glass fibers suitable to be re-used thus closing the Life Cycle for glass fibers: at 500°C the time of air exposure should be 50 minutes or more; at 600°C the oxidative residence time should be about 20 minutes in order to limited the energetic costs.

4. Materials and methods

All the pyrolysis processes presented in this thesis have been conducted in the installed pilot plant [54]. A great optimizing work have done from the first start of the plant to the definition of a standard test.

4.1. Overview of final layout of the pyrolysis system

The pilot plant is composed of several parts, each one with a specific function, as described in Figure 4.1.

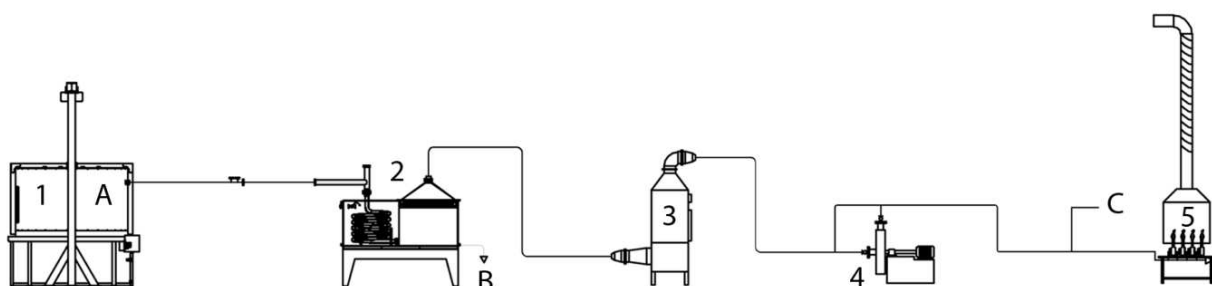


Figure 4.1 - Schematic layout of the experimental pyrolysis pilot plant: 1, pyrolysis chamber; 2, demister; 3, H₂S scrubber; 4, fan; 5, burners; A, collection point of solid residue; B, collection point of pyrolysis oil; C, bleed point of syngas.

The reactor (1) (Figure 4.2) is where the reaction takes place and is projected as a discontinuous static bed reactor. It contains the innovative element of the plant and is covered by an European Patent [53]. The system is easily controllable and safe owing to a hydraulic seal that prevents air from entering the treatment chamber and allows an easier handling of pressure variations inside the reactor. In order to limits the water evaporating during the thermal degradation of the samples, a floating element (Figure 4.3) has been installed to separates the water of the hydraulic seal from the reaction environment.



Figure 4.2 – External view of the reactor in a closed (a) and open (b) configuration.

The reactor has an internal volume of 5.5 m^3 and it is composed of two parts: the first, lower, is a tank containing the hydraulic guard' water and a pedestal that emerges from the water and where the sample is allocated. The second one is a mobile bell whose lifting allows the sample supply and removal of the solid residue at the end of the process (A). The heat necessary to reach the set point temperature is provided by electric resistances for a total power of 2100W, which are housed in a double wall of this latter element.



Figure 4.3 – Floating element inside the reactor.

The reactor is flushed with a stream of N_2 that guarantees the inert atmosphere necessary for the pyrolysis to occur. In the inlet of the reactor is also a current of water useful to maintain a constant level of the hydraulic seal. In case of excessive increase in pressure inside the reaction chamber, the water flows through an overflow and is conveyed towards the discharge.

The gases generated in the process are conveyed outside the reactor and partially condensed in a water cooled coil. The oil and water thus obtained is collected by the demister (2) (Figure 4.4) and picked up at point B at the end of the process and subsequently characterized.



Figure 4.4 – Demister.

The uncondensed gas proceeds encountering a H_2S scrubber (3) (Figure 4.5) and a fan (4) (Figure 4.6), necessary to adjust the pressure of the gaseous stream. Along the line connecting the fan to the burners (5) (Figure 4.7) is located a bleed point for the syngas analysis (C). Different types of indicators and monitoring points for the operating variables are distributed along the entire system and everything is supervised through a centralized electronic control panel.



Figure 4.5 – H₂S scrubber.



Figure 4.6 – Fun.



Figure 4.7 – Gas burners.

4.1.1. Sampling points

The sample is loaded in a discontinuous way on the sample holder inside the reactor. From the pyrolysis is formed a gas that partially condenses in the demister along the process water. The noncondensable proceeds along the line to the burners where it is ignited.

The syngas is sampled and monitored online using a μ -GC positioned between the fan and the burners, before the bottom line valve.

The liquid products (oil and water) are stapled at the end of each pyrolysis cycle through the appropriate valve which is located on the bottom of the demister. The liquid is collected and stored pending the separation of the fractions and characterization.

At the end of each pyrolysis cycle, when the temperature inside the reactor is capable of limiting the evaporation of the water seal, the reactor is opened and the solid residue is collected from the same position where the sample are initially loaded. The solid residue derived from the different pyrolysis cycle are stored pending the subsequent characterization or oxidation treatment.

4.2. Materials

4.2.1. Optimization of pilot plant

The tests aimed to optimizing the pilot plant carried out have been carried out on new car tires of different brand and model, as listed in Table 4.1 The tests were characterized by different conditions of maximum temperature reached, the sensed pressure in the reactor and residence time of the tires in the reactor. The measured values for the variables monitored are shown in the same table.

Table 4.1 - List of runs for pilot plant optimization.

Test code	T (°C)	Brand and model of tires	Number of tires	Weight (kg)	Time (hh.mm)	p (mbar)
1	369,4	Lassa Atracta 155/70R13 79T	0.5	3,10	01.40	Variable
2	397,1	Lassa Atracta 155/70R13 79T	1	6,20	06.15	Variable
3	508,2	Lassa Atracta 155/70R13 79T	1.5	9,40	05.25	Variable
4	500,4	Marix Ecogrip 195/60R15 88T; Bridgestone B 175/65R15 84T	1+1	16,30	04.20	Variable
5	500,4	Lassa Atracta 155/70R13 79T	2	12,40	04.00	Variable
6	488,0	Lassa Atracta 155/70R13 79T	2	12,40	02.04	Variable
7	486,7	Pirelli P6 195/65R15 91H; Hankook Radial 155/65R13 73T	1+1	12,30	02.12	Variable

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8	481,6	Pirelli P7 225/55R16 95V; Pirelli P3000 175/70R13 73T	1+1	15,90	02.09	Variable
9	503,8	Lassa Atracta 155/70R13 79T	1	6,88	08.00	- 7
10	511,4	Lassa Atracta 175/70R13 79T	1	6,72	04.30	- 7
11	483,2	Pirelli P3000 175/70R13 73T; Hankook Radial 155/65R13 73T.	1+2	16,59	02.00	Variable
12	475,7	Lassa Atracta 155/70R13 79T	2	12,96	02.30	- 7
13	494,9	Lassa Atracta 155/70R13 79T	2	13,16	02.30	- 7
14	371,7	Lassa Atracta 155/70R13 79T	2	12,92	02.30	- 7
15	497,4	Lassa Atracta 155/70R13 79T	2	13,02	02.30	- 7
16	496,3	Lassa Atracta 155/70R13 79T	2	12,53	02.30	Variable
17	498,3	Lassa Atracta 155/70R13 79T	2	12,26	02.30	Variable
18	550,7	Lassa Atracta 155/70R13 79T	2	12,44	02.30	Variable
19	496,0	Lassa Atracta 155/70R13 79T	2	12,24	02.30	- 3,5
20	497,2	Lassa Atracta 155/70R13 79T	2	12,82	02.30	- 3,5
21	498,3	Lassa Atracta 155/70R13 79T	2	12,96	02.30	- 7
22	497,6	Lassa Atracta 155/70R13 79T	2	12,65	02.30	- 12
27	N.D.	Bridgestone B250, 175/65R15 84T; Firestone Multihawk, 165/65 R14 79T	1+1	12,42	05.10	Variable
28	467,2	Michelin Energy, 185/60 R15 84H; Michelin Classic, 185/75 R14 PR8	1+1	16,41	01.20	Variable
29	474,3	Firestone Fuel Saver 165/70R13 81T; Firestone Multihawk, 175/70R14 88T	1+1	11,25	01.30	Variable
30	469,5	Lassa Atracta 155/70R13 79T	2	12,33	02.30	Variable
31	500,6	Pirelli P0 195/45ZR16 84Y; Pirelli P3000 165/65R14 79T	1+1	12,98	13.30	Variable
32	495,3	Pirelli P5000 195/45R16 84V; Firestone "F590" 165/70R14 81T	1+1	13,73	02.30	Variable
38	504,9	Lassa Atracta 165/70R13 79T	2	12,32	01.30	- 7
39	515,2	Lassa Atracta 165/70R13 79T	2	12,89	02.30	- 7
40	N.D.	Continental Premium Contact 205/55R16 91V; Yokohama A- Drive 175/65R14 82T	1+1	13,36	01.30	- 7
41	N.D.	Lassa Atracta 175/70R13 84T	2	12,51	02.30	- 7
42	N.D.	Dry run	-	-	02.30	- 7
43	537,6	Lassa Atracta 165/70R13 79T	2	12,93	02.30	- 7
44	517,2	Dry run	-	-	02.40	Variable
45	529,2	Lassa Atracta 175/70R13 84T	2	13,97	02.30	Variable
46	504,0	Lassa Atracta 175/70R13 84T	2	13,94	02.30	- 4

N.D. Not Detected

4.2.2. Standard tests with tires

The tests with end-life tires (ELTs) have been performed on tire sets in different state of wear and with a random mix of brands and models (whose specifics are reported in Table 4.2 with respect to each run conditions) while, in the case of new tires experiments (NT), new car tires Lassa model Atracta have been used. On the basis of the TGA analysis results, both the NT and ELTs tests at 400°C have been repeated twice to check if longer permanence times at this temperature can affect the process. Two tests for each set of tires have been carried out at 450, 550 and 600°C. Several further tests have been carried out at the intermediate temperature of 500°C, that appears the optimal process temperature, sufficient to guarantee complete thermal degradation of whole tires and, while contemporary affording a considerable energy saving. The yields data of the pyrolysis products and composition of syngas have been averaged.

Table 4.2 - List of experimental runs.

Test Code	T (°C)	Brand and model of tires	Number of tires	Weight (kg)
NT400.01	400	Atracta 155/70R13 79T	2	12.92
NT400.02	400	Atracta 155/70R13 84T	3	18.75
ELT400.01	400	Driver Couvier 185/65 R15 88H, Firestone Firehawk 185/65 R15 88H, Driver Couvier 185/65 R15 88H	1+1+1	19.69
ELT400.02	400	Dunlop Sport 205/55 R16 91V, Firestone Firehawk 185/65 R15 88H	1+2	19.12
NT450.01	450	Atracta 155/70R13 79T	2	12.96
NT450.02	450	Atracta 165/70R13 84T	3	20.91
ELT450.01	450	Dunlop Sport 205/55 R16 91V, Bridgestone turaz 195/55 R15 87 H, Firestone fire hawk Tz 88H	1+1+1	22.84
ELT450.02	450	Bridgestone turaz 195/55 R15 87 H, Michelin energy 175/65 R13 82T, Dunlop SP sport 205/60 R13 91H	1+1+1	18.94
NT500.01	500	Atracta 155/70R13 79T	2	12.24
NT500.02	500	Atracta 165/70R13 79T	2	12.32
NT500.03	500	Atracta 155/70R13 79T	2	12.65
NT500.04	500	Atracta 155/70R13 79T	2	12.71
NT500.05	500	Atracta 155/70R13 79T	2	12.82
NT500.06	500	Atracta 165/70R13 79T	2	12.82
NT500.07	500	Atracta 165/70R13 79T	2	12.89
NT500.08	500	Atracta 165/70R13 79T	2	12.95
NT500.09	500	Atracta 155/70R13 79T	2	12.96
NT500.10	500	Atracta 155/70R13 79T	2	13.02

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NT500.11	500	Atracta 155/70R13 79T	2	13.16
NT500.12	500	Atracta 155/70R13 79T	2	13.77
ELT500.01	500	Matador Stella 195/65 R14 79T, Continental Conti Winter Contact 205/55 R16 91H, Pirelli P3000 175/65 R15 84T	1+1+1	19.66
ELT500.02	500	Michelin Energy 165/70 R14 81T, Pirelli P7 205/55 R16 91V	1+2	20.53
ELT500.03	500	Michelin Energy 175/65 R13 82T, Pirelli P7 215/55R16 93V, Firestone CV 2000 195 R14C 102/110 N6 P.R.	1+1+1	22.4
ELT500.04	500	Miratta Lassa 175/70 R14 88H, Pirelli P6000 195/60 R15 88H, Toyo Proxer R32, 205/50 R17 89W	1+1+1	24.24
ELT500.05	500	Bridgestone Turanza ER 300 205/55 R16 91H, Dunlop SP sport 205/60 R13 91H	2+1	25.65
ELT500.06	500	Pirelli P7 205/55 R16 91V, Lassa Impetus revo 205/65 R16 99H, Michelin Primacy HP 225/55 R1797W	1+1+1	26.96
NT550.01	550	Atracta 165/70R13 79T	2	12.93
NT550.02	550	Atracta 175/70R13 84T	2	13.97
ELT550.01	550	Atracta 165/65R13 77T, Atracta 155/70R13 75T, Atracta 165/70R13 79T	1+1+1	19.37
ELT550.02	550	Pirelli P3000 175/65 R15 84T; Pirelli Pzero 205/50 ZR17 93W, Pirelli P3000 165/65 R13 77T	1+1+1	19.63
NT600.01	600	Atracta 155/65R13 73T	3	17.59
NT600.02	600	Atracta 175/70R13 84T	2	13.94
ELT600.01	600	Pirelli Pzero 205/50 ZR17 93W, Michelin Classic 185/75 R14 PR8	2+1	18.65
ELT600.02	600	Michelin Energy 185/60 R15 84H, Michelin Classic 185/75 R14 PR8	1+2	20.54

4.2.3. Tests for producing char

The list of the tests conducted with the objective of produce char for its introduction of in a generic formulation based NR is reported in Table 4.3. The runs have been performed with a feeding of car and truck ELTs selected to represent an average flow of end-life tires. The obtained solid residue from pyrolysis of car and truck tires have been collected separately and properly sampled.

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Table 4.3 - List of runs for the production of char. CT: Car Tires, TT: Truck Tires.

Test Code	T (°C)	Brand and model of tires	Number of tires	Weight (kg)
CT.01	500	Continental Conti Premium Contact 2 205/55 R17; Good Year Excellence 205/55 R17.	1+2	27.62
CT.02	500	Continental Conti Premium Contact 2 205/55 R17; Bridgestone Potenza 235/45 R18; Good Year GT2 175/65 R14; Continental SPORT CONTACT 225/50 R17.	1+1+1+1	33.84
CT.03	500	Bridgestone Potenza 235/45 R18; Yokohama A.Drive 175/65 R14; Formula Energy 185/65 R15	2+1+1	33.00
CT.04	500	Yokohama A.Drive 175/65 R14; Continental SPORT CONTACT 225/50 R17; Maxxis Vitara 510 205/55 R16; Continental Eco Contact EP 155/80 R13; Good Year DURAGRAP 175/65 R15.	1+1+1+1+1	34.12
CT.05	500	Continental Conti Premium Contact 2 195/55 R16; Michelin Pilot Pimacy 205/55 R16; Continental Eco Contact EP 155/80 R13; Yokohama C.Drive 215/50 R17	1+1+1+1	33.47
CT.06	500	Pirelli P2500 euro 165/70 R14; Michelin Pilot Exalto 205/50 R15; Yokohama C.Drive 215/50 R17; Continental Conti Premium Contact 2 195/55 R16	1+1+1+2	34.62
CT.07	500	Yokohama AVS winter 295/65 R15; Pirelli slow control serie 2 255/55 R16	3+1	32.68
CT.08	500	Fulda Crystal Montero 2 175/65 R15; Pirelli slow control serie 2 255/55 R16; GT radial Champiro winter pro 205/55 R16.	2+1+1	31.85
CT.09	500	Fulda Crystal Montero 2 175/65 R15; Pirelli sottozero winter 210 205/55 R16; GT radial Champiro winter pro 205/55 R16	1+2+1	33.47
CT.10	500	Nokian WR 205/55 R16; Lassa snoway 185/65 R15; GT radial Champiro winter pro 205/55 R16.	1+2+1	31.84
CT.11	500	Fulda Crystal Montero 2 175/65 R15; Continental Conti Eco Contact 3 185/60 R15; Good Year DURAGRAP 175/65 R15; Lassa snoway 185/65 R15.	2+1+1+1	33.48
CT.12	500	Cleber Dynaxer HP3 195/60 R15; Cleber C801T 155/80 R13; Yokohama winter 195/65 R15; Good Year Ultragrip8 185/65 R15; Fulda Crystal 175/65 R15.	1+1+1+1+1	33.78
CT.13	500	Milestone winter 195/70 R15; Good Year Ultragrip8 185/65 R15; Lassa snoway 185/65 R15; Fulda Crystal 175/65 R15	1+1+1+2	35.08
TT.01	500	GT Radial 315/70 P22,5	0.5	26.87
TT.02	500	GT Radial 315/70 P22,5	0.5	25.97
TT.03	500	GT Radial 659+ 315/70 P22,5	0.5	25.47

4.2.4. Tires pyrolysis char – Material Safety Data Sheet

The translated version of the MSDS for tires pyrolysis char is reported.

The present Material Safety Data Sheet is compiled according to the requirements of Annex II to the European Directive (CE) n. 1907/2006/EC. ARTICLE 31 of the EUROPEAN PARLIAMENT AND COUNCIL

1. PRODUCT & COMPANY IDENTIFICATION

Product name:	Faenza Char
Synonym:	Tire Char, Pyro Black, Pyro Carbon
Chemical family:	Petroleum Derivative
Chemical formula:	Not applicable
Supplier:	Curti S.p.A Via Emilia Ponente 750, 48014, Castel Bolognese (Ra) - ITALY
Emergency number	+ 39-377-7040957
Use of substance	Used as filler/pigment in tyres/rubber, plastic goods/inks/coatings etc.
Non-recommended uses	Everything not explicitly permitted under Use of substance

2. HAZARDS IDENTIFICATION

Not a hazardous substance or preparation according to EC-Directives 67/548/EEC or 1999/45/EC and their various amendments and adaptations.

Not a dangerous substance according to Regulation CLP-(CE) n. 1272/2008.

USA: this material is classified as dangerous according to OSHA Regulations.

ROUTES of EXPOSURE	
Inhalation, Eye contact, Skin contact	
Potential health effects	
Eye contact:	may cause mechanical irritation. Irritating, but will not permanently injure eye tissue.
Skin contact:	may cause mechanical irritation, soiling and drying of skin
Sensitisation:	no case of sensitization in humans has been reported.
Inhalation:	Dust may be irritating to respiratory tract
Ingestion:	Dust has been reported as annoying
Carcinogenic effect:	There are no known human carcinogenic effects related to the PAH content of material. Recent research has shown that the PAH is not released from material in biological fluids and thus not available for biological activity.
Medical conditions Aggravated by Exposure	Asthma, respiratory disorders

3. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical name:	Faenza Char---
Composition:	Carbon: 84-87% Hydrogen: 2.8-3.5% Nitrogen: 0.2-0.5% Oxygen: 4.5-5.5% Sulphur: 1.5-3.0% Metals: 3.0-8.5% Benzo (α) pyrene <1 ppm
TWA	3.5 mg/m ³

4. FIRST AID MEASURES

Skin contact:	Remove contaminated clothes and take precautions to avoid breathing the resulting dust. Wash skin with mild soap and water. If symptoms develop seek medical attention. Wash contaminated clothes if necessary.
Inhalation:	Take affected person out in fresh air. If necessary restore normal breathing condition through standard first aid measures.
Eye contact:	Flush eyes with large amount of water. Seek medical attention if symptoms develop.
Ingestion:	Drink 1-2 glasses of water. Seek medical attention if symptoms develop.

5. FIRE-FIGHTING MEASURES

Extinguishing media:	Use foam, carbon dioxide (CO ₂), dry chemical or water spray
Extinguishing media NOT to be used	Do not use water under pressure
Protection of firefighters:	Products of combustion include carbon monoxide (CO), carbon dioxide (CO ₂) e oxides of sulphur. Wear full protecting firefighting gear including self-contained breathing apparatus.
Specific Hazards:	It may be not obvious that material is burning unless the material is stirred and sparks are apparent. Material that has been on fire should be observed closely for at least 48 hours to ensure no smouldering material is present. Burning produces irritant fumes.
Flash Point	Not determined

ACCIDENTAL RELEASE MEASURES

Personal precautions:	Wet material produces slippery working surfaces
Methods for cleaning up:	Use water to reduce dust. A vacuum equipped with HEPA (High Efficiency Particulate Air) filtration is recommended. Do not create dust cloud using a brush or compressed air. Pick up and transfer to properly labelled containers.
Environmental precautions:	Material poses no significant environmental hazards. Minimize contamination of sewage water, soil, ground water, drainage systems or bodies of water.

6. HANDLING AND STORAGE

Handling:	Avoid contact with skin and eyes. Wash exposed skin daily. Provide ventilation at machinery and places where dust can be generated. Fine dust may cause electrical shorts and is capable of penetrating equipment unless tightly sealed. Take precautionary measures against static discharge. If hot work (welding, torch curring etc) is required the immediate work area must be cleared of carbon product and dust.
Storage:	Store in a dry place away from ignition sources and strong oxidizers. Do not store together with volatile chemicals as they may be absorbed onto product. Keep in properly labelled containers.

7. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls	Use process enclosures and, or exhaust ventilation to keep airborne dust concentrations below the occupational exposure limit..
Administrative Controls:	Specific training must be provided to the assigned personnel before one-off or routine handling of the material.
Personal Protective Equipment	
Respiratory Protection	An approved air-purifying respirator (APR) may be used where airborne concentrations are expected to exceed occupational exposure limits.

Hands Protection	Wash hands and other exposed skin with mild soap and use skin cream to prevent skin drying. All purpose protective gloves can be used to safeguard hands.
Eye Protection	Use protection glasses
Skin Protection	Wear standard protective gear to minimise skin contact. Work clothes shall not be taken home and should be washed daily
General hygiene conditions	Emergency eye wash kits and safety showers should be at hand. Wash hands and face thoroughly with mild soap before consuming food or drink.

8. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	Black powder/pellets
Odor	None/petroleum-like
pH	4-9
Apparent Density	0.300-0.350 g/cm ³
Humidity ASTM D7582	0-1%
Percent volatiles ASTM D7582	5-9%
Solubility in water	<1%
Autoignition temperature	>140°C
Minimum ignition temperature	520-600°C
Ignition Energy	>1 kJ
Burn velocity	> 45 seconds, (not classified as highly flammable)
Explosion limits in air	Upper %: not determined Lower %: 50 g/m ³ (dust)

9. STABILITY AND REACTIVITY

Stability	Stable under normal ambient conditions
Incompatible Materials	Strong oxidizers such as bromates, chlorates and nitrates
Hazardous decomposition products	Carbon monoxide,
Hazardous polymerizations	Will not occur

10. TOXICOLOGICAL INFORMATION

Acute toxicity	
Acute Oral LD50	> 8000 mg/kg (rats)
Acute Dermal LD50	Not available
Acute Inhalation LC 50	Not available
Primary Skin Irritation	0.6/8 light irritation (rabbit)
Primary Eye Irritation	Non irritative (rabbit)
Subchronic toxicity	
Rat, inhalation, duration 90 days, NOAEL	Quantity: 1.0 mg/m ³ Target organs: lungs Effect: inflammation, hyperplasia, fibrosis
Chronic toxicity	
Rat, oral, duration 2 years	No tumors
Mouse, oral, duration 2 years	No tumors
Mouse, dermal, duration 18 months	No skin tumors
Rat, inhalation, duration 2 years	Target organs: lungs Effect: inflammation, fibrosis, tumors
Carcinogenicity	
Not available	
Sensitivation	
Not available	
Reproductive effects	
Not available	
Epidemiology	
Cumulative exposure to material may result in small decrements in lung function	

11. ECOLOGICAL INFORMATION

Ecotoxicity	
Aquatic Toxicity LC50, 96 hours, Brachydanio Rerio (zebrafish)	>1000 mg/l
Acute Water Flea Toxicity EC50, 24 hours, Daphnia Algae Magna (water flea)	>5600 mg/l
Acute Algae Toxicity EC50, 72 hours, Scenedesmus Subspicatus	>10000 mg/l
Mobility	Not soluble in water
Bioaccumulation	Not expected

12. DISPOSAL CONSIDERATIONS

Product must be disposed of in a suitable manner according with the regulations of the appropriate state and local authorities.

Contaminated packaging materials must be disposed of with the material

13. TRANSPORT INFORMATION

Material is not considered dangerous to transport.

14. REGULATORY INFORMATION

Not hazardous substance according to EC Directives 99/45/EC and their various amendments and adaptations.

15. OTHER INFORMATION

The product described in this MSDS is currently under development and additional data may be provided as it is discovered. The information in this MSDS was obtained from sources we believe accurate, as of this date.

4.2.5. Carbon Fibers Reinforced Composites

The epoxy composite samples selected to represent the range of CFRCs scraps have been supplied by Ri-Ba Composites srl and include both uncured (from now on referred to as “prepreg”) and relative cured scraps coming from different stages of the manufacturing process and containing the same kind of carbon fiber (Toray T700S, 12K). All samples have been pyrolytically treated without any further treatment, meaning that no shredding nor crushing has been applied.

Virgin fibers, used for comparative purpose, have been obtained cutting down Unidirectional Fabric UC 301 purchased from SAATI and based on the same Toray T700S 12K used for prepregs and cured composites. The two components epoxy resin used for chopped fiber composites production is the ElanTech EC157/W61 Polymer/Hardener system purchased from Elantas.

4.2.6. Fiberglass

The glass fiber-reinforced polyester composite samples (GFRPs) are cutout scraps coming from manufacturing process of polyester laminates with glass fiber MAT, supplied by Vetroresina S.p.A. The samples have been received in the form of sheet rolls with thickness 2.5 mm, width about 250 mm and a length up to 3 m. The samples are composed of an isotropic glass fiber mat reinforcement (12.5 μm of diameter) with a polyester matrix covered with a protective low density polyethylene (LDPE) thin film on one side that represents 4.4wt% of the overall material weight.

All samples have been pyrolyzed without any further treatment, meaning that no shredding nor crushing have been applied.

4.3. Experimental procedure

4.3.1. Pyrolysis experiments

The plant is designed for discontinuous operation, a standard cycle is then composed of various subsequent phases.

In a typical run, new and end-life tires are placed into the reactor. After closing the lid, the reaction chamber is flushed with nitrogen in order to remove air, then the system is heated at 8°C/min rate up to the set point, and then maintained at the desired temperature for a total residence time of 150 mins. The tires pyrolysis experiments have been performed isothermally

at different temperatures, namely 400, 450, 500, 550 and 600°C, as defined upon preliminary TGA investigation.

The tests performed in order to obtain char for its introduction in a generic formulation based NR have been performed heating at 8°C/min rate up to 500°C, and then maintained at the desired temperature for a total residence time of 150 mins.

In a typical run, CFRCs scraps are placed into the reactor. After closing the lid, the reaction chamber is flushed with nitrogen in order to remove air, then the system is heated at 8°C/min rate up to the set point, and then maintained at the desired temperature for a total residence time of 150 mins. The CFRCs pyrolysis experiments have been performed isothermally at different temperatures, namely 450, 500, 550 and 600°C for the cured scraps and 500, 550 and 600°C for the prepreg, as defined upon preliminary TGA investigation.

In a typical run, fiberglass scraps are placed into the reactor. After closing the lid, the reaction chamber is flushed with nitrogen in order to remove air, then the system is heated at 8°C/min rate up to the set point, and then maintained at the desired temperature for a total residence time of 150 mins. The fiberglass pyrolysis experiments have been performed isothermally at different temperatures, namely 500, 550 and 600°C.

4.3.2. Post-Pyrolysis Oxidation treatment

The oxidation step has been carried out on the solid residue derived from the pyrolysis of CFRCs cured scraps at 500°C and 600°C. The fibers, about 1Kg, as obtained from pyrolysis, have been inserted in a muffle furnace at 500°C or 600°C and isothermally kept for different residence times (10, 20, 30, 40, 50 and 60 mins) in order to determine a suitable oxidation step duration. The recovered fibers have been characterized by Scanning Electron Microscopy (SEM) and Raman spectroscopy.

The oxidation step has been carried out on the solid residues derived from the pyrolysis of fiberglass. The glass fibers with a superficial carbonaceous residue, as obtained from pyrolysis, have been inserted in a muffle furnace at 500°C or 600°C and isothermally kept for different residence times (10, 20, 30, 40, 50 and 60 mins) in order to determine a suitable oxidation step duration. The recovered glass fibers have been characterized by Scanning Electron Microscopy (SEM) and Raman spectroscopy [63].

4.3.3. Chopped Carbon Fiber Reinforced Composites production

Carbon Fibers recovered from pyrolysis batches carried out on cured composites (Re-CF), either pristine or muffle oven treated for oxidation (Table 4.4), have been cut at about

25mm length and mixed with two-components epoxy resin mixture in a 1:1 ratio for the production of Re-CCFRCs. The resin formulation has been prepared according to the supplier Technical Data Sheet. The resin/Re-CF mixture has been inserted into a 210 x 170 x 5 mm mold and hot-press cured at 45 bar and 100°C for 40 minutes. The same procedure has been performed with virgin fibers, in order to prepare Virgin- Chopped Fiber Composites. After cooling down to RT, each composite panel has been cut into 100x15 mm stripes in order to perform thermal and mechanical characterization [63].

Table 4.4 - Nomenclature and process conditions of chopped carbon fibers reinforced composites production [63].

Sample	Fiber	Pyrolysis Conditions	Post-treatment	Curing cycle
VF	Pristine	-	-	110°C, 40 min., 45 bar.
Re500	Recycled	500°C	-	110°C, 40 min., 45 bar.
Re600	Recycled	600°C	-	110°C, 40 min., 45 bar.
Re500-P500-60	Recycled	500°C	500°C, 60 min.	110°C, 40 min., 45 bar.
Re600-P600-30	Recycled	600°C	600°C, 30 min.	110°C, 40 min., 45 bar.

4.4. Methods

At the end of each test, the pyrolysis solid and liquid products have been properly handled, then steel, oil, and char have been weighed. The syngas fraction has been obtained by difference.

Thermogravimetric (TGA) analysis has been carried out using a TA Instruments SDT-Q600 instrument. Preliminary pyrolysis experiments have been carried out on approximately 10 mg of material in nitrogen atmosphere from RT to 700°C at 10°C/min heating rate.

The analysis of the oxidizing step simulation have been performed under air flow heating at a rate of 25°C/min from RT to 500 and 600°C and then kept in isotherm. Measurements carried out to characterize the chopped fibers composite have been run from RT to 600°C heating at a rate of 10°C/min in air and leaving the sample 15 mins in isotherm at 600°C.

The particular characteristic engineering plant involves co-condensation of oil and process water. For this reason, after the bleed from the demister, the two fractions have been separated by means of a centrifuge operating at 4200 rpm for 6 minutes. The oil fraction has been characterized by GC-MS analysis using a Thermo FOCUS GC, coupled to a DSQ mass spectrometer as detector and equipped with a Supelco SPB™ fused silica capillary column.

The kit has allowed the identification of compounds that characterize the lighter oil's fraction. Benzene, toluene, ethylbenzene, p-xylene and styrene have been quantified by calibration curves of the individual compounds of known concentration. The dynamic viscosity has been determined at 25°C using a digital Brookfield viscometer – Model DV-II +, spindle “I” with a rotational speed of 100 rpm. The values have been compared with those obtained for a common commercial diesel fuel. To assess the effect of shelf life on the physical properties of the oil, the analysis of density and dynamic viscosity of some significant samples has been repeated after 6 and 12 months. Simulated distillation using thermogravimetric method (SimDis TGA) has been performed on oil samples of about 15 mg in platinum pans suitable for liquids (heating rate of 5°C/min from room temperature (RT) to 500°C in a nitrogen flow of 100 mL/min).

The gaseous phase has been analyzed *in situ* with a Micro-Gas Chromatograph Agilent 490 Micro-GC placed on-line in the pilot plant so no active sampling is required. Two columns have been used for analysis: a Molsieve 5 Å (MS, 20 m) with molecular sieves made with zeolites as stationary phase and argon as carrier gas. The MS column has been held at 80°C throughout the experiment. This asset has been designated for separating H₂, O₂, N₂, CO and CH₄. The second column is a PoraPLOT U (PPU, 10 m) with divinylbenzen-ethylene glycol/dimethylacrylate as stationary phase and helium as carrier gas. The PPU column has been held to 90°C throughout the experiment. This asset has been designed to separate H₂S, CO₂, C₂H₄, C₂H₆ and hydrocarbons up to C₃, with the possibility of detecting even the C₄. The detector used by the device is a Thermal Conductivity Detector (TCD). Quantification has been performed by comparison against a blend of gases of known composition. The calorific value of the gas (GCV) has been calculated, according to the UNI 7839, by means of the obtained composition.

The char obtained from tires pyrolysis has been manually separated from the steel wires. The char produced through similar tests has been collected and then sampled. Its characterization has the aim to evaluate its possible use as a fuel or as a raw material. Ashes, water and volatile materials contents have been determined by TA instruments SDT Q600 according to the ASTM D 7582. According to ASTM D 1552-07, the elemental composition CHN-O/S has been used to calculate the higher heating value (Gross Heating Value, GHV) and lower heating value (Net Heating Value, NHV). X-Ray Fluorescence spectra have been recorded on a PANalytical AxiosMAX Advanced XRF Spectrometer, equipped with a rhodium X-ray tube target, set to a power of 2.4 kW in order to quantify the sulfur and Zinc contents and detect the presence of heavy metals. Finally, the determination of the total surface area has

been carried out by nitrogen adsorption at -196°C using a Carlo Erba SORPTY 1750 equipment which uses the simplified BET model.

In order to investigate the morphological aspect of the fibers after pyrolysis and pyrolysis/oxidation treatments, micrographs have been taken with a Scanning Electron Microscope (SEM) ZEISS EVO 50 EP in Environmental mode with ≈ 100 Pa pressure in the chamber. The EDX probe is an Oxford Inca EDS 350.

Raman spectra on fibers have been recorded with an Ar^+ laser light source (514.5 nm). The Raman spectrometer is also equipped with a Leica DMLM Renishaw 1000 RAMAN Micro-Spectrometer equipped with microscope (objectives 5x, 20x, and 50x), a rejection filter (notch or edge), a monochromator (1200 lines/mm) and a charge-coupled device thermoelectrically cooled (203 K) detector.

Tensile tests have been carried out at room temperature with an Instron-type tensile testing machine (REMET TC10), with crosshead speed of 5 mm/min and initial gauge length of 50 mm.

5. Conclusions

Taking into account the priorities on waste management imposed by the European legal framework together with the need to limit the extraction of primary resources, in this work an innovative pyrolysis pilot plant has been successfully developed with the aim of recover secondary raw materials from a waste characterized by a single flow of reject management, in particular tires, carbon fibers reinforced prepreg and cured scraps and glass fiber-reinforced polyester composite scraps.

The technology involves the pyrolysis of non-shredded waste in presence of steam, which is due to the presence of an hydraulic seal that guarantees an extreme explosion-proof process carried out in an anti-infiltration environment.

The pilot plant optimization was primarily aimed at reducing the water evaporation from hydraulic seal without neutralize its benefits and at investigating the effects of pressure, sample residence time and process temperature as process variables.

The obtained data demonstrated that temperature appears as the most influential variable and, independently from the type of waste, it can be correlated not only to the degree of degradation, but also to the product yields and composition. In particular, the ratio oil/syngas increases with temperature and the syngas is enriched in light compounds (H_2 , CH_4 , C_2 , and C_3).

The pyrolysis of whole new and end-life tires have been conducted in the 400-600°C range. The lower temperature is insufficient for the complete degradation of the tires, regardless the residence time. By conducting the pyrolysis above 450°C, the process leads to: an oil fraction rich of high commercial value compounds, thanks to the presence of high amounts of BTX, with high GCV and low sulphur content (1wt%). The characterization of the oil fraction, repeated after one year, shows negligible changes during this period.

- A syngas fraction enriched with hydrogen and methane;
- a char fraction (40wt%) with high GCV and promising mechanical properties when used in 20/80 blends with N330 carbon black;
- a steel fraction, completely recoverable through a specific recovery chains.

In summary, both the oil and syngas fractions can be used to completely sustain the production process obtaining as added-value products both char and steel that can re-enter the market as secondary raw materials, with energetic surplus.

Considering the advantages brought by this technology, a continuous multi-batch plant able to process from 1.5 to 4.0 tonnes per hour have been designed. The project aims to implement the first industrial application and actions for market replication, of an innovative technology for the treatment of ELTs, capable of improving the quality of recycled materials. The project presents solid elements of business development and market replication, as it aims at spreading an innovative technology with clear economic and social benefits, which has already been tested up to the pilot stage, and therefore presents limited technological risks.

The pilot plant has also been used to provide some preliminary assessment of the possibility of applying a coupled pyrolysis/oxidative process to CFRCs wastes, both prepregs and cured scraps, in order to produce carbon fibers as a secondary raw materials to be re-used for new composites production. The pyrolysis tests have been carried out in the 500-600°C for prepregs and 450-600°C range for cured scraps. The gaseous and liquid by-products can sustain about 75% of the process energy requirement by the pilot plant although it is non-optimized in terms of energy balance. The CFs recovered after pyrolysis appear covered by a layer of amorphous carbonaceous derivatives and the resin results non completely degraded. All this residue can be removed through a further thermal treatment in air at high temperature between 500-600°C (oxidation). The CFs recovered after the oxidation process have been re-used to provide Chopped Carbon Fiber Reinforced Composites with performances comparable to those obtained with pristine fibers.

Finally, the same pilot plant has been used to dispose GFRPs scraps. The pyrolysis process, conducted in the 500-600°C range, yielded an oil ($\approx 20\text{wt}\%$) and a gas ($\approx 40\text{ wt}\%$) that can be both used again to sustain the process with an energetic performance able to cover the 75% of the process energy requirement and recover a solid residue ($\approx 40\text{wt}\%$) composed of glass fibers covered by a thin carbonaceous layer. It have been also demonstrated that, by a further oxidation treatment at temperature between 500-600°C, it is possible to obtain clean glass fibers suitable to be re-used thus closing the Life Cycle for glass fibers: at 500°C the time of air exposure should be 50 minutes or more; at 600°C the oxidative residence time should be about 20 minutes in order to limited the energetic costs.

5.1. Future work

Boosted by the current regulatory framework, in the short term the need for technologies leading to the production of secondary raw materials through pyrolysis of tires

and CFRCs will be growing faster and faster. Hence, to further develop the technology presented in the present thesis few issues should still be addressed.

It is first required the optimization of the char properties of in order to increase its commercial value and then further reducing the breakeven times. The char, ground to different particle sizes, will be pelletized to improve its handling and then used in blends with standard carbon blacks in the production of NR and EPDM compounds.

Contemporary, a research comparing different tires pyrolysis plant configurations by Life Cycle Assessment will be necessary.

Moreover, the opportunity to make substantial changes to the pilot pyrolysis plant in order to plan an *in line* thermal treatment carried out directly on the hot solid residue at the end of the pyrolysis process should be evaluated.

The production of prototypes with recycled fiber cannot be separated from the optimization of the curing cycle of the matrix which will be optimized and carried on in closely controlled conditions in order guarantee the best fiber/matrix interface adhesion possible.

The reinforcing effect of the recovered CF, compared to virgin fibers, must be deepened in order to identify the boundary conditions for the use of recycled fiber. Finally, based on statements of intent by the companies involved in this project, commercial collaborations for the production of chopped recycled CF may also be launched.

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