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Experimental evaluation of the pyrolysis of plastic residues and waste tires

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Abstract. The paper presents the design of the experimental apparatus developed in order to analyse the performance of a prototype of a pyrolysis system for the exploitation of the plastic residues of industrial processes and the end-of-life tires. The small-scale pilot prototype is specifically designed for carrying out an experimental campaign aimed at determining the influence of different plastic types on the yield and on the quality of the liquid oil, gas and char obtained in the pyrolysis process. The study investigates the effect of different mixtures of various plastic products mainly made of polyethylene, styrene butadiene rubber, nylon, and natural rubber. The prototype is equipped with a control system able to monitor the main operating parameters of the process, such as the pyrogas pressure and temperature as well as the temperature inside the reactor where the pyrolysis takes place. The monitored variables are employed for deriving correlations among the operating conditions and the yield of the pyrolysis process. Moreover, SPME-GC/MS analysis were performed on different gas samples to estimate the main compounds that are contained in the syngas in comparison to the different plastic wastes analysed. Thus, the emissions of the small-scale prototype are evaluated. The results obtained by means of the experimental campaign performed on the test rig were used to carry out the economic assessment of an integrated pyrolysis system for the exploitation of the plastic residues from an industrial plant.

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Abbreviations

Acronym	Description
SPME	Solid-phase microextraction
GC	Gas chromatography
MS	Mass spectrometry
PSW	Plastic solid waste
HTL	Hydrothermal liquefaction
LPG	Liquified petroleum gas
DAQ	Data acquisition system
NDIR	Non dispersive infrared sensor
ECS	Electrochemical sensor
DVB	Divinylbenzene
CAR	Carboxen
PDMS	Polydimethylsiloxane
SBR	Styrene-butadiene rubber
PE	Polyethylene
NR	Natural rubber
ICE	Internal combustion engine

Symbols and units

Symbol	Description	Unit
C_i	Cash flow at i -th year	€/y
Inv	Investment cost	€
C_{tot}	Operating cost of the combined system	€/y
$R_{net-meti}$	Savings in terms of reduced cost	€/y
S_i	Revenues for the energy efficiency certificates	€/y
NPV	Net present value	€
Wacc	weighted average cost capital	€
EBITDA	Earnings before interest, taxes, depreciation, and amortization	€

1 Introduction

The attention towards the efficient use of energy sources has increased substantially in the recent years, due to the increasing awareness of the limits regarding the fossil fuels [1].

Thus, the scientific community and the Institutions are challenged in developing green energy systems capable to replace the fossil fuels.

Numerous technologies for producing bioenergy heat and power already exist, such as solid wood heating installations for buildings and biogas digesters for power generation as well as large-scale biomass gasification plants are also employed for heat and power generation [2,3,4,5].

In the last fifty years, plastic has attracted considerable interest as a material for the enhancement of the properties of different products in many sectors, such as packaging, building and construction, automotive, electronics, biomedical and others. In today's scenario, plastics production has reached about the 311 million tonnes in 2014 [6] determining a continuous growing in waste accumulation every year. Plastic solid waste (PSW) is being produced on a massive scale worldwide and its production crosses the 150 million tonnes per year globally, as presented in [7]. The European strategy for plastics in a circular economy [8] reports that 25.8 million tonnes of plastic waste are generated in Europe every year. Due to its plentiful environmental impact, the plastic waste is becoming a key priority and different technologies for treating the plastic residues already exist.

Al Salem et al. (2009) [9] presented a review on the different routes for recycling and recovery the plastic solid waste. They identified four different strategies for the PSW treatment such as re-extrusion, mechanical treatment, chemical treatment and energy recovery. According to statistics established in Europe [8], less than the 30 % of the plastic waste is collected for recycling, while the landfilling and incineration rates are the 31% and 29 % respectively. Even though the percentage of the plastic waste disposed to landfill has slightly decreased over the last decades, it is still very high. Al Salem et al. [9] presented the mechanical recycling as the most common technique for the recycling of plastic waste. In 2017, Ragaert K. et al. [10] presented a description of the main steps of the mechanical recycling which includes collection, sorting, washing and grinding of the material. Their study highlights that polymers will degrade during the mechanical recycling; this degradation occurs during lifetime and by reprocessing. For this reason, many materials can be reused a limited number of times before they cannot be longer chemically active to produce products with certain chemical properties [11].

The amount of plastic disposed to landfill that is not treated via mechanical recycling can be used for energy recovery. In [8], it was estimated that the production and the incineration of the plastic give rise globally to approximately 400 million tonnes of CO₂ a year. Therefore, the European Commission has introduced specific measures and procedure [12] to reduce the negative effect on the environment from the incineration of hazardous waste. New sustainable processes of recycling have emerged, defined as chemical recycling [13], a process that convert plastic into liquids or gases which can be used as a fuel or as feedstock to produce new plastic products [14]. Most of the studies available in literature present the hydrothermal liquefaction, gasification, and the pyrolysis processes as the advanced thermal treatment methods for the reduction of the plastic waste.

Hydrothermal liquefaction (HTL) is a process that emerged for the valorisation of biomass; today it is applied to the plastic waste to provide energy recovery [15]. The hydrothermal treatment of different plastic types has been investigated in [16] where the influence of the batch holding time and the temperature on the yield, composition and quality of oil was determined.

Gasification is a process that operates at high temperatures, i.e. 600-800°C, based on the thermo-chemical decomposition of the plastic into a synthesis gas that is suitable for the electricity production or for transportation fuel [17]. In 2013, A. Brems et al. [18] confirmed the importance of the introduction of the gasification process of the plastic solid waste into a valid recycling route of the PSW producing some syngas rich in H₂ and CO.

Pyrolysis is the thermal decomposition process that occurs in the absence of oxygen and produces energy from waste in three different phases: solid biochar, liquid oil and syngas [19]. In literature, many studies have been conducted regarding the influence of various types of plastics on the product yield. In [20] the set-up parameters that affects the pyrolysis process are identified and they include temperature, type of reactors, residence time and pressure. The pyrolysis process operates at high temperatures, in the range 300-1000 °C [21, 22,23].

In 2011, Kumar et al. [24] observed that the degradation of the polyethylene started at 400 °C and the maximum weight loss is at 427.7 °C. In [25] the polystyrene pyrolysis was analyzed and the maximum yield of liquid oil was reached at 425 °C. Kan et al. [26] investigated the pyrolysis process of natural and synthetic rubber. The study determined the syngas composition by chromatographic techniques and demonstrated that the syngas is mainly composed by hydrogen and carbon monoxide; H₂ was observed between 350 and 525 °C for the natural rubber, while in the range 300-500°C hydrogen is the dominant species for the synthetic rubber. The heating and melting phenomena of plastics in a semi-batch pyrolysis reactor have been studied numerically in [27]. The results of the simulations were validated against experimental measurements and the average relative error between the experiments and the simulations was lower than the 8%: Burra et al [28] investigated the co-pyrolysis of pinewood and different types of plastic waste using polypropylene, polyethylene terephthalate and polycarbonate in different mass fractions, The results of the co-pyrolysis were compared with the pyrolysis of individual components and non-additive synergistic effects from co-pyrolysis were revealed. The study demonstrated an increase in carbon conversion efficiency and volatiles yield during co-pyrolysis compared to individual component pyrolysis. In literature there are many studies that investigate different technologies and layout of the systems for the pyrolysis. In particular, the pyrolysis systems can be divided in two different configurations. The first layout is composed by a reactor, a distillation column, a condenser and a reboiler; the latter configuration consists of a reactor and a combustion chamber [19]. In the second design there is no liquid production because there is no condenser.

The aim of the present paper is the design of a test rig for investigating the pyrolysis of different mixtures of plastic waste. The experimental campaign focuses on the pyrolysis of polyethylene, styrene butadiene rubber, nylon and natural rubber. The prototype is composed by a pyrolysis reactor, an heat exchanger, a separator and a filter. This configuration enables to produce energy from different plastic wastes obtaining syngas, oil and solid biochar. The test rig is equipped with an acquisition system that monitors the main variables of the process by means of temperature and pressure sensors placed in characteristic position of the prototype. As a consequence, it is possible to investigate the thermal behavior of the process and the influence of the operating temperature on the yield of the process. Different analytical methods were used to characterize the chemical composition of the gases produced by the process. The content of O₂, CO, CO₂, NO, NO₂, CH₄, H₂ was determined using an infrared sensors industrial analyzer. Moreover, gas samples were collected by using tedlar gas sampling bags. These samples were then analyzed by SPME-GC/MS to evaluate the composition of the syngas generated by the combustion process, to assess the sustainability of the technology. Furthermore, the analyses of the condensed fuel oil inside the separator have been carried out. The physical properties of the three fuel oils are investigated to evaluate the influence of the three different treated plastic wastes.

Finally, the application of a pyrolysis integrated system is evaluated for an industrial company that produces plastic pipes; the proposed plant aims at valorizing the plastic residues of the manufacturing process producing char, fuel oil and pyrogas. The pyrogas and liquid oil fuels are exploited in a bi-fuel engine to generate electrical energy. As in [29], the heat from the exhaust gases is recovered to decrease the thermal energy demand of the pipes manufacturing process. The economic analysis of the proposed plant is addressed, and the payback period of the pyrolysis plant resulted to be lower than 7 years when considering a constant increase of 15% for the cost of the plastic waste disposal. To the best of Authors' knowledge this type of analysis has not been carried out on a real industrial application. Furthermore, the specific characteristics qualify the proposed analysis as an example of circular economy that cannot be found in literature for this type of process industry.

2 MATERIALS AND METHODS

In this section, the test rig has been analyzed into detail focusing of the description of the main components and the monitoring systems developed to investigate the main variables of the pyrolytic process. The different plastic types tested have been presented.

2.1 Pilot plant

2.1.1 Layout

Figure 1 depicts the experimental test rig developed for the experimental tests and the locations of the temperature and pressure sensors installed in the system. The experimental apparatus includes three main parts: a reactor, a condenser/separator, and a filter for the treatment of the exhaust generated by the syngas combustion.

The main unit is the reactor where the pyrolysis process takes place, and it is composed by two detached cavities. The burner is placed in the external chamber and the air is maintained in circulation to transfer the heat uniformly to the internal cavity. The chemical transformation of the plastic waste occurs in the internal cavity, which is completely sealed in order to avoid syngas leakages. The sealing action is performed by two different gaskets: the first made by silicone and the second one composed by an insulate fabric.

The internal cavity measures 1,5 mm thick and the internal volume is approximately 1m³ that allows a material maximum load equal to 100 kg. A heat exchanger and a separator are connected downstream the reactor. The heat exchanger cools down the syngas to condensate the liquid part, which is stored in the separator. The remaining syngas flows to the torch; in the real system the non-condensed syngas is used to power the reactor.

A scrubber system is added before the exhaust chimney to filter the syngas gases generated by the syngas combustion.

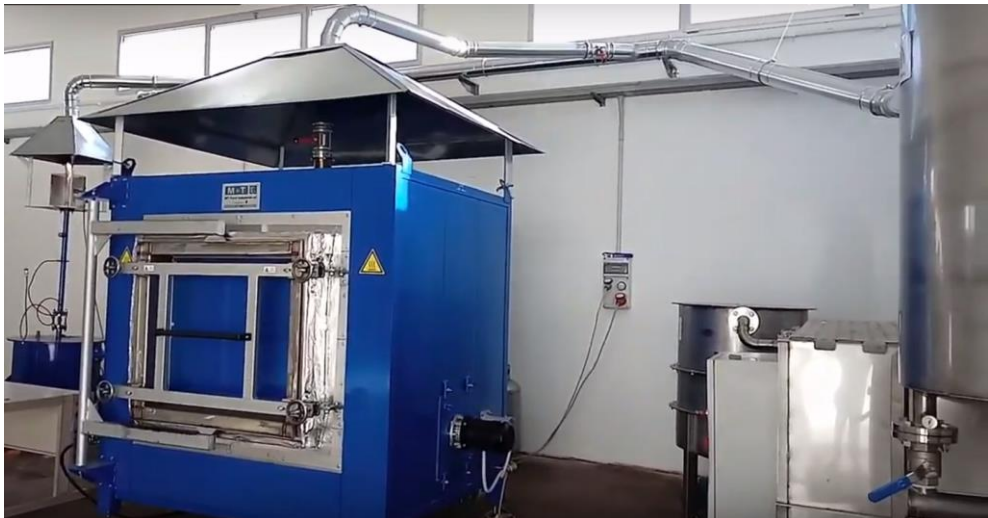


Figure 1-Experimental test rig

2.1.2 Monitoring System

The sensors installed in the system are employed to monitor the main variables of the process. The temperature and pressure are measured by eight thermocouples and four pressure

transducers placed in characteristic part of the system. The temperature distribution inside the internal chamber is monitored by three different thermocouples (A); these sensors enable to investigate the suitable temperature for the pyrolysis reaction to maximize the yield of the process. Temperature (D) and pressure (E) sensors are installed to register syngas variables at the reactor outlet. The thermocouple (F) measures the temperature of the water inside the heat exchanger. Furthermore, two thermocouples (G, I) and two pressure transducers (H, L) are positioned upstream and downstream the separator to monitor the temperature and pressure of the syngas respectively before and after its separation from the liquid phase. Finally, a thermocouple (B) and a pressure transducer (C) are placed at the chimney in order to measure the exhaust temperature and pressure generated by the LPG burner. Figure 2 shows the piping and instrumentation diagram of the pyrolytic process while Table 1 lists the operating range and the accuracy of the measuring instruments employed to characterize the system

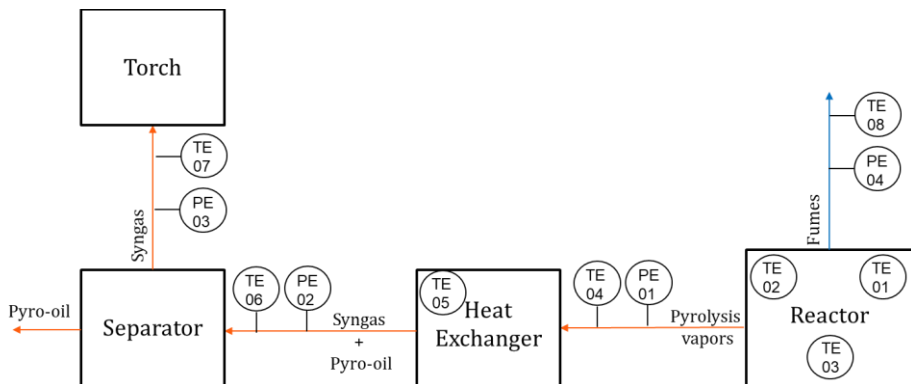


Figure 2 – P&Id of the experimental test rig

Sensor type	Operating range	Accuracy	Reference letter in Figure 1
Thermocouples	-270÷1370 °C		TE01, TE02, TE03, TE04, TE05, TE06, TE07, TE08
Pressure sensor	-1÷1 bar	<0.02% FS	PE01
Pressure sensors	0÷0.5 bar	<0.02% FS	PE02, PE03, PE04

Table 1-Specifications of the sensors installed.

The data acquisition is carried out using a National Instrument DAQ module integrated by a customized LabView interface, displayed in Figure 3. Through this interface the user is also able to control remotely all the working parameters of the system.

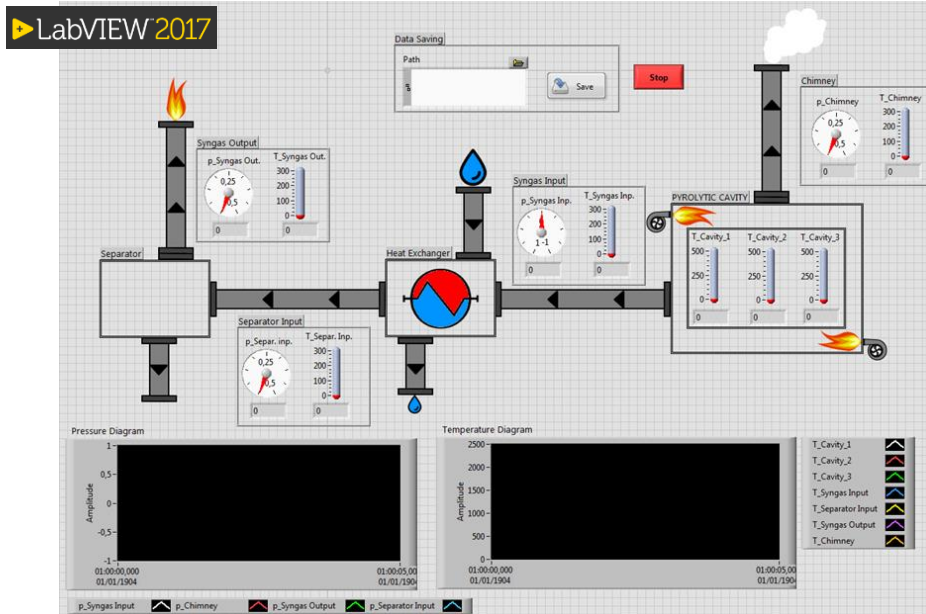


Figure 3- LabVIEW monitoring interface.

2.1.3 Industrial gas analyzer

The composition of the syngas at the outlet of the separator is analyzed by means of an industrial gas analyzer. The system acquires the composition of the syngas in real time, i.e. 1 sample every 10 seconds. The hardware technology is based on infrared sensors (NDIR) and electrochemical sensors (ECS) that enable the identification of the elements that compose the syngas. The molecules analyzed by the system are O₂, CO, CO₂, N₂, CH₄, C_xH_y, H₂ and they are measured as a percentage of the total mass. In Figure 4 the industrial gas analyzer is shown.



Figure 4-Measuring instrument installed on the pilot plant.

2.1.4 SPME-GC/MS analysis

To obtain detailed information on the composition of the syngas produced during the experimental tests and, as a consequent, on the emissions of the small-scale prototype, different samples are collected during the whole duration of the experimental tests. Tedlar bags are used to collect the gas samples. Their waterproofing properties and chemical

inertness guaranteed the physical integrity of the collected samples, which remained uncontaminated and unchanged without changes over time, even during storage. The analyses of the collected samples are carried out by SPME-GC/MS technique.

2.1.4.1. Solid phase microextraction

A 50/30 mm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco) was used to collect and concentrate the gas analytes sampled by the tedlar bags. Before the use, the fiber was conditioned following the manufacturer's recommendation. The bag sampling was performed manually, exposing the fiber for 30 minutes at room temperature (23°C)

2.1.4.2. SPME-GC/MS analysis

Then GC/MS analyses were carried by means of a TraceISQ QD Single Quadrupole GC/MS (Thermo Fisher) equipped with a VF-5MS capillary column (30 m, 0.25 mm, 0.25 µm, Agilent). The instrumental conditions are reported below.

Injection time: 1 min; helium was used as the gas carrier; injection mode: split; split flow: 120 ml/min.

Oven program: 40° C for 2 min; then 10° C/min to 300° C for 20 min; Run Time 48 min. MS transfer line: 300° C. Ion source: 300° C. Ionization mode: electron impact: 70 eV. Acquisition mode: full scan (50-1000 m/z).

2.2 Experimental tests

An experimental campaign has been carried out to investigate the pyrolysis of different plastic types. The collected plastic samples consist of waste tyres, grocery bags, fabrics and vulcanized pipes that are mainly made of polyethylene, styrene butadiene rubber, natural rubber and nylon. The collected samples are used individually and as a mixture.

Table 4 **Error. L'origine riferimento non è stata trovata.** lists the three experimental tests carried out in this study.

Test	Typology	Main Compounds	Quantity [kg]
#1	Waste tyres	Styrene-butadiene rubber (SBR)	34.5
#2	Grocery bags	Polyethylene (PE)	11.5
#3	Fabrics and rubberized pipes	Nylon, SBR, natural rubber (NR)	21.7

Table 2-Typology of plastics used in the experimental runs

The pyrolysis process operates approximately between 400-420 °C and a reaction time of 3-4 hours is used for all experiments depending on the composition of the materials of each batch cycle. In the test rig, the chamber where the pyrolysis process takes place is directly connected with the external ambient: indeed, a hole on the backwall of the furnace enables the syngas to flow through the heat exchanger and the torch.

After the warmup phase of the system, the PSW starts transforming in syngas; as a consequence, the pressure inside the cavity increases and the syngas can gradually flow out from the cavity to the torch, where it is burnt, and the exhaust are finally conveyed to the scrubber system.

3 RESULTS

3.1 Temperature and pressure analysis

The most important operative parameters, in particular temperature and pressure, were analyzed in the experimental campaign; the time dependent temperature curves registered by the eight thermocouples are shown in Figure 5 (a), (b) and (c) for the three experimental tests reported in **Errore. L'origine riferimento non è stata trovata.**

During the experimental test #1 the pyrolytic reactor is loaded with waste tires (4 SUV tires). The complete cycle lasted about 3h and the transients related to the temperatures and pressures recorded by the sensors are presented in Figure 5 (a). The temperature measured at the chimney (orange line) shows the temperature evolution inside the external chamber. The temperature set in the burners' control panel is 400 °C; this setpoint is decreased to 350 °C after being constant to 400 °C for 15 minutes. Consequently, the temperatures measured by the three thermocouples installed into the internal chamber grow up to 400 °C and remain quite stable till the end. The curve named syngas input shows the temperature of the syngas at from the outlet of the internal cavity. This temperature remains lower than 100 °C and then gradually grows when the syngas starts to flow out.

The experimental test N#2 is conducted by introducing waste plastic bags into the inner cavity. The trend of the temperatures recorded during the test is shown in Figure 5(b).

After a warm-up phase of the reactor of approximately 1 hour, the temperature is maintained at 350°C for approximately 60 minutes; thus, the temperature is increased of 100 °C to allow the complete development of the pyrolytic process in the final section. It can be noticed the first phase of shutdown and cooling of the pilot plant with the consequent reduction of all temperatures.

The experimental test #3 is conducted by introducing vulcanized pipes and rubberized and metallic fabric into the inner cavity. The trend of the temperatures recorded during the test are represented in Figure 5(c). After a first heating part of the pyrolytic reactor, the last one is kept at a constant temperature to facilitate the thermo-chemical degradation of all the materials loaded. As can be seen from Figure 5(c), the increase in temperature measured at the syngas input coincides with the beginning of the formation of the syngas phase.

Figure 5(d) represents the trend of the pressures registered by the four pressure transducers during the 4h duration of the #2 experimental test and saved by the LabVIEW software.

The trend of the pressures can be defined constant, following an initial settling phase. Indeed, the sensors, at the beginning of the test, register a pressure caused by the air remaining inside the system, which is driven by the hot vapors coming out of the pyrolytic reactor. Instead, in the conclusive part of the process when the pressure produced by the syngas is no longer significant, the pressures monitored inevitably drop.

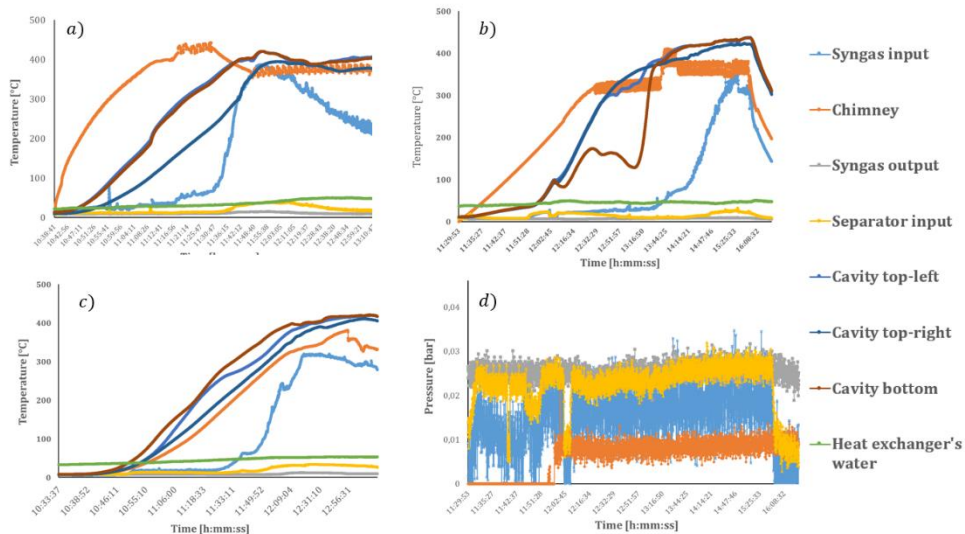


Figure 5-(a) Waste tires pyrolysis temperatures graph, (b) Polyethylene bags pyrolysis temperatures graph, (c) Rubberized fabric and vulcanized pipes waste pyrolysis temperatures graph, (d) Polyethylene bags pyrolysis pressures graph

3.2 Yields

Figure 6 shows the product yields in terms of liquid oil, char and pyrogas for the three plastic wastes investigated. The pyrolysis temperatures at which the plastic wastes have been chemically degraded are in the range of 400–420 °C for every experimental test.

For the calculation of the products obtained from each test we weighed the resulting char and oil (sensitivity of the balance: 0.1kg), while the mass of the syngas had been calculated by difference with the initial weight of the pyrolyzed product.

In experimental test #1 (34.5 kg of waste tires), the char and the residues remained in the cavity are respectively 12.59 kg (36.5% wt) of char and 5 kg (14.5% wt) of steel belts (used to reinforce SUV tires). The raw fuel oil collected in the separator is 12.4 kg (36% wt). Indeed, the pyrolysis of waste tires generally aims to maximize the yield of the liquid-phase product, because of the valuable chemicals obtained from it. The mass balance of the system enables to exactly the amount of syngas generated by the pyrolytic process and burned by the torch: 4.48 kg (13% wt). Those results are perfectly in line with literature data reported by Martinez et al. [30], Li et al. [31], Antoniou et al. [32], Aylon et al.[33].

Thermal pyrolysis of grocery bags (polyethylene) during the experimental test #2 produces a high yield of liquid oil (65%) while the gas and the char produced are 26% wt and 9% wt respectively. According to literature data, Salem and Lettieri[34], Onwudili et al[35], Sogancioglu et al[36], pyrolysis of polyethylene produced more oil compared to tires pyrolysis. we found a slightly higher percentage for char probably due to contamination of the initial sample with sand and dust. The residues of the last experimental test, i.e. #3, into the internal chamber can be resumed as follows: 4.9 kg (23% wt) of char and 4.9 kg (23% wt) of steel fibers (used to reinforce pipes and fabrics). Into the separator 8.15 kg (38% wt) of raw fuel oil are collected. Finally, the amount of syngas generated by the pyrolytic process

can be estimated into 3.6 kg (16% wt). In that case, comparison with literature data were not possible in reason of the really particular composition of our test sample, which, as far as we know, has never been studied. The best comparison we can do is with tires, which are quite similar. Echoing comments above made, comparing our test data with what reported by [30], [31], [32], [33], the yield percentage we found are absolutely in line with literature.

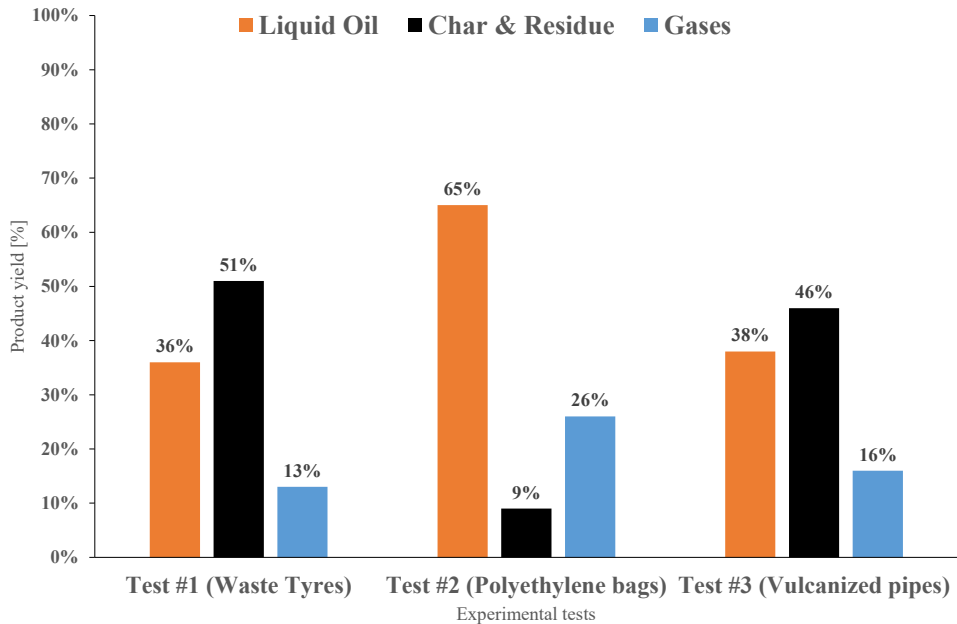


Figure 6-Effect of plastic waste types on product yields

3.3 Composition

3.3.1 Syngas composition: infrared sensors Industrial gas analyzer

The following tables report the composition of the syngas registered by the industrial gas analyzer at the outlet of the separator during the three experimental tests: the volumetric composition of each molecule is the average value detected along the entire test, since the syngas starts flowing out of the system till the end. In Table 3 **Error! L'origine riferimento non è stata trovata.** the composition of the syngas related to the experimental test #1 is presented. Usually, the gas-phase products from the pyrolysis of waste tires are paraffins (that were clearly visible on the bottom surface of the pipes), olefins, hydrogen, carbon oxides and other compounds in a small percentage. H₂ and CH₄ occupied the majority of the volumetric composition while CO, CO₂ and O₂ represent the 15% of the total volume of the syngas. Thus, the syngas is characterized with a high calorific power.

O ₂ (%v)	N ₂ (%v)	H ₂ (%v)	CO (%v)	CO ₂ (%v)	CH ₄ (%v)	C _x H _y (%v)	Total (%v)
1	4	25	5	9	55	1	100

Table 3-Volumetric syngas composition of the Test #1.

The volumetric composition of the pyrogas related to the experimental test #2 is presented in Table 4 **Errore. L'origine riferimento non è stata trovata.**. The volumetric composition of the pyrogas is slightly different from the one mentioned above. Indeed, the percentages of CH₄ and H₂ are increased while the volumetric compositions of CO and CO₂ are reduced. Moreover, the syngas relative to the pyrolysis of PE bags is also characterized by the 7% of N₂. Consequently, in this case the calorific value will be reduced compared to the previous one due to the different concentrations found.

O ₂ (%v)	N ₂ (%v)	H ₂ (%v)	CO (%v)	CO ₂ (%v)	CH ₄ (%v)	C _x H _y (%v)	Total (%v)
1	7	17	4	6	59	6	100

Table 4-Volumetric syngas composition of the test N#2.

In Table 5 **Errore. L'origine riferimento non è stata trovata.** the volumetric composition of the pyrogas obtained in test #3 is presented.

In the table below H₂ and CH₄ occupied most of the volumetric composition; CO and O₂ represent the 8% of the total volume of the syngas.

O ₂ (%v)	N ₂ (%v)	H ₂ (%v)	CO (%v)	CO ₂ (%v)	CH ₄ (%v)	C _x H _y (%v)	Total (%v)
1	5	24	7	8	53	2	100

Table 5-Volumetric syngas composition of the test #3.

Moreover, the heating value of the three different syngas obtained in each of the three experimental tests can be addressed has been determined by means of the industrial gas analyzer. As shown in Table 6, the syngas produced by each experimental test is characterized by similar lower heating values; the highest value is obtained for Test #2 since the polyethylene released more fuel gases with the respect to the other plastics investigated. A good agreement has been found between the experimental syngas heating values and the values that can be found in literature.

Test	Lower Heating value [MJ/kg]
#1 (Tires)	33.4
#2 (Polyethylene)	36.2
#3 (Rubberized pipes)	32.9

Table 6-Syngas lower heating values.

3.3.2 Syngas and exhaust gases composition: SPME-GC/MS technique

The collected samples were also analyzed by SPME-GC/MS technique to obtain qualitative information on the chemical composition of the gases.

Here, only the analyses related to the samples of syngas and exhaust fumes regarding the experimental test #2 (PE bags) are reported, because this case turned out to be the most interesting concerning the quantity of gas that can be extracted from the plastic waste.

The GC/MS chromatograms of the two samples and a blank (the fiber after thermal cleaning) are showed in Figure 7.

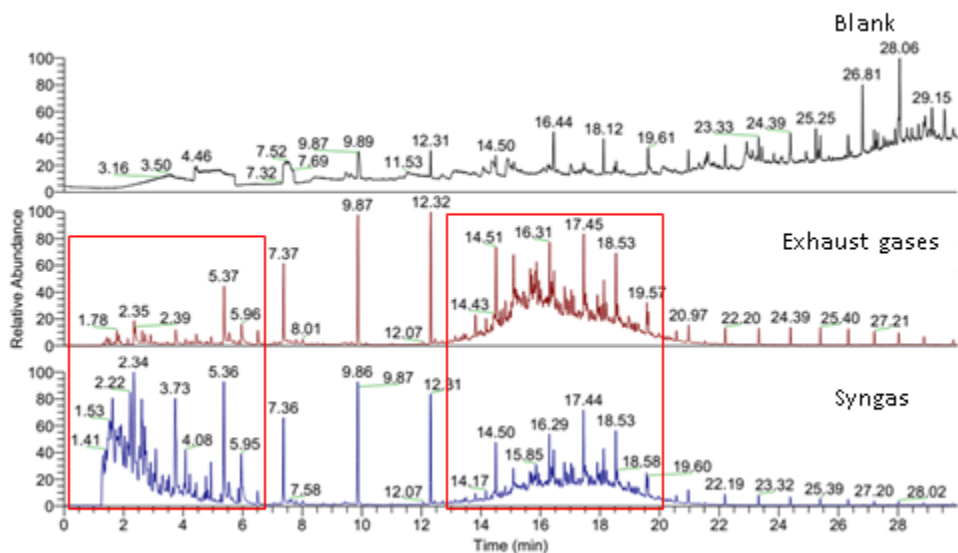


Figure 7-Chromatograms of the blank and of the two analyzed samples.

As shown in Figure 7, the GC/MS chromatographs of the two samples are very similar and show two interesting zones (red squares). Even though there are qualitative analyses, it is worth noting that comparing the first zone (GC retention time 1.31-6.51 min) of the two chromatographic profiles syngas sample showed more intense signals than exhaust gases one. Table 7 shows the list of the analytes of the first zone of Figure 7, identified by match with NIST 2014 library.

RT (min)	Match	Samples
1.31	Methylenecyclopropane	Syngas, exhaust gases
1.33	Perfluorododecanoic acid*	Syngas, exhaust gases
1.41	Perfluorinated*	Syngas, exhaust gases
1.44	3-hydroxy-2-methylpentanale	Syngas, exhaust gases
1.54	Perfluoro-1-heptene	Syngas, exhaust gases
1.77	Hexene	Syngas, exhaust gases
1.77	Perfluorinated*	Syngas, exhaust gases
1.81	Pentane	Syngas, exhaust gases
1.85	Perfluorinated*	Syngas, exhaust gases
1.90	Perfluorinated*	Syngas, exhaust gases
2.14	Perfluorinated*	Syngas, exhaust gases

2.34	Benzene	Syngas, exhaust gases
2.39	3-methyl-4-penten-2-ol	Exhaust gases
2.63	Heptene	Syngas, exhaust gases
2.72	Perfluorinated*	Syngas, exhaust gases
2.91	Perfluorinated*	Syngas, exhaust gases
3.03	Perfluorinated*	Syngas, exhaust gases
3.09	Cyclohexylmethane	Syngas, exhaust gases
3.47	Perfluorinated*	Syngas, exhaust gases
3.73	Toluene	Syngas, exhaust gases
4.09	Octene	Syngas, exhaust gases
4.23	Octane	Syngas, exhaust gases
4.54	Perfluorinated*	Syngas, exhaust gases
4.59	Dimethyl-heptane	Syngas, exhaust gases
4.77	Trimethyl-hexene	Syngas, exhaust gases
4.94	Dimethyl-heptene	Syngas, exhaust gases
5.26	trimethylcyclohexane	Syngas, exhaust gases
5.36	Ethyl-benzene	Syngas, exhaust gases
5.54	Xylene	Syngas, exhaust gases
5.86	Nonene	Syngas, exhaust gases
5.95	Styrene	Syngas, exhaust gases
6.51	Cumene	Syngas, exhaust gases

Table 7-List of analytes in the 1-6.5 min interval.

The second zone of Figure 7 (GC retention time 13-20 min) mainly contains heterocycles and long chain esters.

3.3.3 Fuel oil composition

Finally, the compositions of the fuel oil collected directly from the separator have been analyzed for each experimental test. Table 8 shows the main compounds found in the oil of the three experimental tests.

Parameter analyzed	Test 1 (Tyres)	Test 2 (Polyethylene)	Test 3 Rubberized pipes)	UoM
Water <i>ISO 3733:1999</i>	< 0.05	0.1	0.5	% m/m

Sediments <i>ISO 3735:1999</i>	0.01	0.25	0.29	% m/m
Viscosity @ 50°C <i>UNI EN ISO 3104:2000</i>	1.651	2.446	2.286	mm ² /s
Density @ 15°C <i>UNI EN ISO 12185:1999</i>	838.4	825.3	904.2	kg/m ³
Ashes <i>UNI EN ISO 6245:2005</i>	0.002	0.005	0.231	% m/m
Pour point <i>ISO 3016:1994</i>	12	27	21	°C
Sulfur <i>ASTM D 1552-16e1</i>	0.54	< 0.1	0.54	% mass
Hydrogen <i>ASTM D 5291-16</i>	12.9	13.1	10.5	% mass
Higher Heating value <i>ASTM D240-17</i>	44.543	45.310	36.124	MJ/kg
Lower Heating value <i>ASTM D240-17</i>	41.805	42.530	33.895	MJ/kg

Table 8-Fuel oil properties

From the analyses relative to these samples, the fuel oils obtained during tests #1 and #2 were found to be quite aligned. The lower and heating values of the oil obtained by Test #3 are lower compared with the lower and higher calorific values of Test #1 and Test #2; Comparing data found in these tests with some found in literature, see in particular Yaqoob et al [37], [38], Vihar et al [39], Sharma et al [40] and Jantaraska et al [41], we can say we are aligned with them.

In particular they proposed water content < 0.5% wt, viscosity between 2 and 5 mm²/s, density in the range of 800 – 900 kg/m³, sulfur between 0.1% and 1.5%.

The only data we found not aligned with literature is LHV of Test 3 (rubberized pipes), which is slightly lower than the lowest value we found (38MJ/kg), reported by Sharma et al [40].

4 ECONOMIC ASSESSMENT

The economic assessment of a pyrolysis combined plant for the exploitation of the rubber residues from a rubber producing company was carried out. The industrial case study considered in this analysis concerns a manufacturer of plastic fabrics and rubberized pipes and tubes; the annual disposed residues from the manufacturing process are approximately 1100 tons per year. Table 9 reports the main operating costs of the plant and the major the company studied and a major expense is due to the production scrap disposal.

Often, good quality single-component plastic waste can be resold on the recycling market, generating an economic income for the company, but the disposal of this particular type of plastic waste, made of chlorinated and sulphured composed materials, involves large treatment costs, and the company pays a fee of 400 €/t for material disposal (data provided by the company). This mean an annual cost of approximately 440.000 Euro per year (2020).

Parameter	Value	UoM
Specific cost for plastic residues disposal	0.4	Euro/kg
Total cost for plastic residues disposal	440 000	Euro/year
Specific cost for electric energy	0.16	Euro/kWh
Specific cost for gas methane	0.34	Euro/m ³

Table 9-Main operating parameters of the industrial company considered in the analysis

The proposed system for the conversion of the plastic waste to energy is the combined pyrolysis-bi-fuel engine-exhaust filtration system plotted in Figure 8. First, the production scrap from the rubberized pipes manufacturer is converted into pyrogas by means of a pyrolytic reactor. The conversion efficiency of the pyrolytic process is estimated considering the results of the experimental test #3 (test which had been conducted with company rubber easte), see Figure 6. Thus, the product yields are: 16% wt of syngas, 38% of fuel oil, 23 % of char and 23 % of steel residues.

The first outputs of the pyrolytic process are the char and the other residues (mainly steel) remained in the reactor after the thermal process; the economic valorization of these outputs is neglected in the economic assessment of the combined system, due to their low margin profitability. The high temperature pyrogas flows in the condenser system that cools down the gas; thus, the fuel oil is condensed. The gas and the fuel oil are then treated in the filtration system; during the treatment process approximately the 20% of the products, gas and oil, is removed. These filtration wastes are a cost included in the economic assessment since they must be disposed to landfill. The purified gas and oil fuels are converted into electricity and heat by means of a bi-fuel internal combustion engine cogeneration unit. A bi-fuel engine has been selected for this application because it is an efficient way to cope with the time varying production of the pyrogas which can be compensated with the oil. The pyrogas can be exploited once it is formed, avoiding the need of tanks and high pressure compression.

Thus, the electric energy is produced by the engine while the heat recovered from the ICE is mostly employed in the manufacturing process, reducing the energy demand.

The electric energy conversion efficiency is equal to the 30 % while the waste heat recovery efficiency is the 40 %.

Finally, the exhaust gases generated by the ICE are filtrated and purified.

The calculated reduction for the plastic waste to be disposed and the decrease of the amount of purchased electric and thermal energy are considered for the calculation of the economic analysis of the energy system.

The following equations calculate the cash flow at the beginning of the investment and at the i -th year respectively. The values of the cash flows are determined by including the operating costs of the combined system ($C_{tot, ent}$) and the savings in terms of reduced costs for the plastic waste disposal and for the energy that has still to be purchased (R_{net_meti}); the revenues from the energy efficiency certificates incentives have been also included in the analysis (S_i).

Equation (3) determines the net present value (NPV) based on the weighted average cost capital (wacc)

$$C_i = -Inv \quad (1)$$

$$C_i = -C_{tot} + R_{net_meti} + S_i \quad (2)$$

Equation (3) determines the net present value (NPV) based on the weighted average cost capital (wacc); the profitability of the investment is calculated over a period of 15 years (estimated life time of the combined system).

$$NPV = \sum_0^{years} \frac{C_i}{(1+wacc)^i} \quad (3)$$

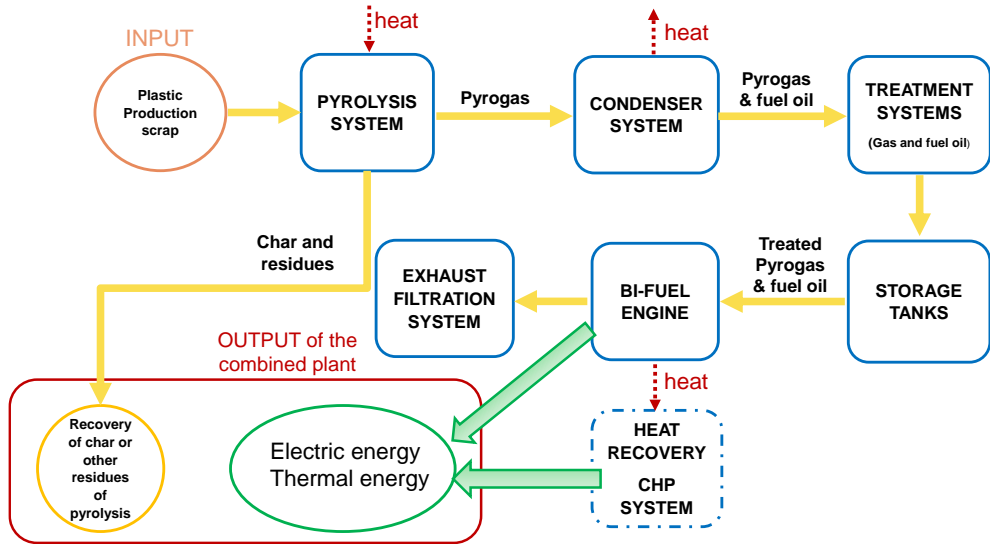


Figure 8-Layout of the considered combined plant

Considering the process yields of the pyrolytic process mentioned above, a constant plastic waste input of 1100 tons per year and the systems conversion efficiencies from manufactures' datasheets, the main outputs of the combined system have been estimated and reported in Table 10.

It can be noticed that the fuel oil production is 334.4 tons per year while the pyrogas production is more than 140 tons per year. Therefore, accounting for the literature lower heating values for the oil and the gas, the total net electric energy production is approximately 1,290,000 kWh per year; it is shown the net electric energy production because the energy consumption of the combined system has been already taken into account.

Table 10 displays also the thermal energy production which is used to reduce the gas methane demand exploiting the heat produced by the ICE to generate vapour required for the industrial process.

Finally, the final plastic residues disposed to landfill are calculated to be more than 100 tons per year: these wastes are generated by the filtration process.

Parameter	Value	UoM
Fuel oil yield	334.4	t/y
Pyrogas yield	140.8	t/y
Electric energy production from fuel oil	1,114,667	kWh/y
Electric energy production from pyrogas	352,000	kWh/y
Total Net electric energy production	1,290,667	kWh/y
Thermal energy production from fuel oil	1,486,222	kWh/y

Thermal energy production from pyrogas	469,333	kWh/y
Total thermal energy production	1,955,556	kWh/y
Disposed final residues from oil filtration	83.6	t/y
Disposed final residues from oil filtration	35.2	t/y

Table 10-Main outputs of the combined plant

The economic assessment of the pyrolytic integrated system is analysed by comparing the energy costs of the proposed solution with the reference operation.

Table 11 shows the savings that can be achieved with the installation of the pyrolytic reactor and the operational costs of the system.

Table 11 reports a remarkable saving for the reduction of the energy purchase greater than 270,000 euro per year when considering both the electric and thermal energy while the avoided cost for the plastic waste disposal is even greater (440,000 Euro per year).

Nevertheless, a significant profit of the proposed system is due to the energy efficiency incentives, i.e. 104,000 Euro per year.

The costs of the system are mainly due to energy demand for the heating process of the reactor, the employee cost for the operation of the system, maintenance and consumables; there is also a cost for the final waste disposal of the gas and oil after the filtration system.

Finally, the VAN for the first year is equal to 360,337 €.

Revenues	Value	UoM
Avoided cost from the plastic waste disposal	440,000	Euro/y
Avoided cost from electric energy purchase	206,507	Euro/y
Avoided cost from thermal energy purchase	69,591	Euro/y
Energy efficiency certificates	104,000	Euro/y
Total Revenues	820,097	Euro/y
Expenses	Value	UoM
Gas methane consumption of the reactor	37,840	Euro/y
Employees	230,400	Euro/y
Maintenance and consumables	144,000	Euro/y
Final waste disposal	47,520	Euro/y
Total Expenses	459,760	Euro/y
EBITDA	360,337	Euro/y

Table 11-Profit and loss statement of the pyrolytic system

For the NPV calculation, the investment cost for the proposed combined plant is equal to 3.6 million Euro. Figure 9 shows the trend of the net present value over the lifetime of the system (15 years). The assumption of the economic analysis is that the costs for the energy procurements and the cost for the plastic disposal are constant for each year and equal to the values reported in Table 9.

Under this hypothesis, the payback period lies between the eleventh and twelfth year; the final revenue is larger than 1 million Euro.

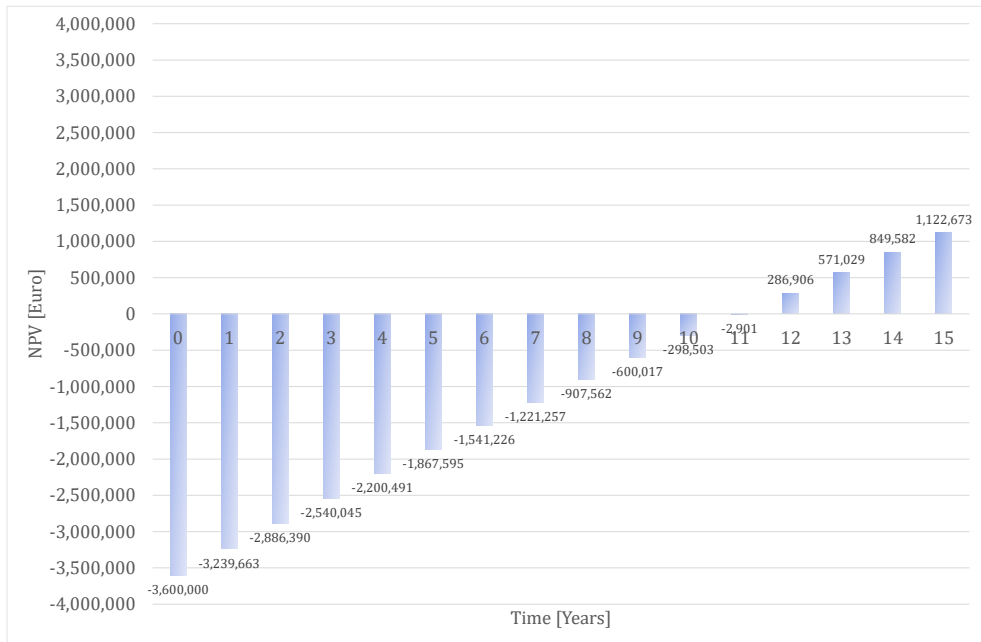


Figure 9- NPV calculation for the proposed combined plant

In the last five years, the cost for the plastic waste disposal has been characterized by significant fluctuations, as it can be noticed in Figure 10. Indeed, the cost was equal to 0.15 Euro per kilogram in 2015; the maximum value has been reached in 2020 with a cost of 0.4 Euro per kilogram. A significant increase has been registered between the years 2017 and 2018 (+28.7%), but the highest gain (+61 %) recorded in 2019.

Under these oscillations, it is not valuable the assumption of a constant cost of the disposal for the plastic residues, but it is difficult estimating which will be the trend in the following years. For these reasons, the NPV has been calculated assuming different increases in the price of the plastic residues disposal with the respect to the price registered in 2020: +5%, +10 %, +15 %.

Table 12 reports the main economic performance (payback and final revenues) of the investment for each cost increased analysed.

If the cost registers a constant increase of 5% per year, the payback period is reduced of 2 years with the respect to the scenario mentioned above (Figure 9) and it lays between the eight and ninth year; the final revenue, i.e. at the fifteenth year, is greater than 3.5 million Euro and it is approximately the investment cost of the combined plant (3.6 million Euro).

In the second scenario, +10 % of increase, the final revenue is larger than 7.1 million Euro, which is approximately two times the initial investment.

Finally, an increase of 15% determines an economic performance in terms of final revenues which largely triplicates the initial investment since the final revenues are equal to 12,776,118 Euro.

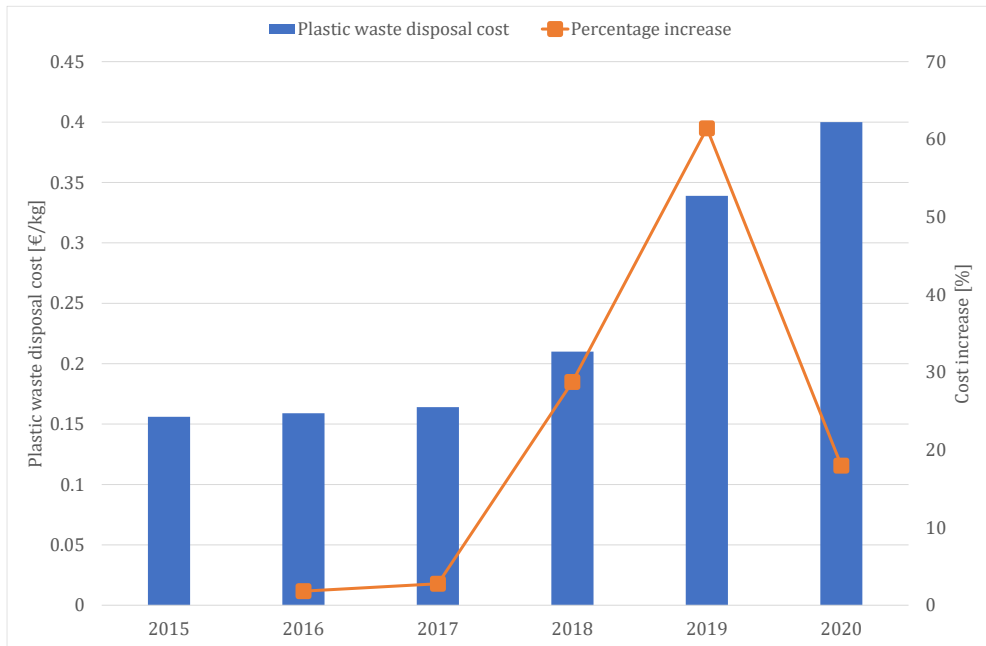


Figure 10- Trend of the cost for the plastic waste disposal over the last 5 years.

Price Increase for plastic waste disposal	Payback of the investment [year]	Final Revenue [Euro]
+5 %	Between eighth-ninth year	3,504,250
+10%	Between seventh-eight year	7,157,999
+15%	Between sixth-seventh year	12,776,118

Table 12-Economic performance of the investment for different plastic waste price increase

4.1 DISCUSSION

In this paper, the proposed economic analysis concerns an extremely particular case. We have studied the case of a really large manufacturer of special plastic materials. The very high cost of disposing of waste material makes the feasibility study of an internal treatment and recovery plant particularly interesting. In particular, the high volume of waste produced makes the application of a medium-scale pyrolysis plant profitable.

Another peculiarity of the type of company is the constant demand during the year and the day for both electricity and heat, thus allowing the installation of a cogeneration system to maximize energy recovery from pyrolysis products and opening up to the possibility of obtaining further state incentives. In addition, the carbon black (char) obtained during the process would be reused internally in new compounds, further increasing the economic convenience.

All the above-mentioned characteristics qualify the proposed analysis as an example of circular economy that cannot be found in literature for this type of process industry.

5 CONCLUSIONS

In this paper a pyrolytic reactor prototype has been developed and implemented.

Real time acquisition and temperatures and pressures monitoring in the main area of the system was achieved thanks to the installation of appropriate sensors and the development of an interface, through the LabVIEW software, for their management. The temperature and pressure transients for each experimental test conducted were presented.

The percentages of the output products were monitored and compared with those already present in literature and a good agreement was found. The composition of the syngas was analyzed in real time thanks to the industrial analyzer and values in line with those found in literature were obtained. The polyethylene pyrolysis (experimental test #2) generates the highest yield in term of syngas and the lowest with regards the char; the fabrics and rubberized pipes has the highest yield (38 % wt) of fuel oil while the waste tires' pyrolysis generates the 51%wt of final residues. The heating values of the syngas measured during the three experimental tests follow the same trend.

Finally, the composition of the syngas and the exhaust gases for the experimental test #2 was investigated by means of SPME-GC/MS technique and the characteristics related to the fuel oil obtained in each of the three experimental tests have been presented.

The results of the experimental campaign carried out on the pyrolytic prototype have been used to evaluate the integration of a pyrolytic combined system in a plastic pipes manufacturing company. The company considered in the analysis is characterized by a constant plastic waste scrap of approximately 1100 tons per year. The feasibility study focuses on the valorization of this plastic waste by means of the pyrolysis system: the gas and fuel oil obtained by the proposed plant are used to generate heat and electricity.

Finally, the economic assessment of the proposed plant is evaluated, and the payback period of the investment resulted to be more than 11 years under the hypothesis of a constant cost for the plastic waste disposal of 0.4 Euro per kilogram.

When considering an increase of the plastic disposal cost, the investment becomes more profitable. Indeed, an increase of the 10 % generates a final revenue of more than 7 million euro while the 15 % increase determines a revenue of approximately 12.7 million euro.

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