

2.1.2 Monitoring System

The sensors installed in the system are employed to monitor the main variables of the process.

The temperature distribution inside the internal chamber is monitored by three different thermocouples (A).

A temperature (D) and a pressure (E) sensor 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 to measure the exhaust temperature and pressure generated by the GPL burner.

Table 1 lists the operating range and the accuracy of the measuring instruments employed to characterize the system.

Table 1. Specifications of the sensors installed

Sensor type	Operating range	Accuracy	Reference letter in Figure 1
Thermocouples	-270÷1370 °C		A, B, D, F, G, I
Pressure sensor	-1÷1 bar	<0.02% FS	E
Pressure sensors	0÷0.5 bar	<0.02% FS	C, H, L

Table 2. Experimental tests analysed

Test	Typology	Main Compounds	Quantity [kg]
#1	Waste tyres	SBR	34.5
#2	Grocery bags	PE	11.5
#3	Fabrics and rubberized pipes	Nylon, SBR, NR	21.7

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

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 hardware technology is based on infrared sensors (NDIR) and electrochemical sensors (ECS) that enable the identification of the elements that compose the syngas.

The elements analyzed by the system are O₂, CO, CO₂, NO, NO₂, CH₄, H₂ and they are measured as a percentage of the total mass.

2.1.4 SPME-GC/MS analysis

In order to obtain a more accurate analysis about the composition of the syngas produced during the experimental tests and the emissions of the small-scale prototype, different samples are collected during the whole duration of the experimental tests. Thanks to its waterproofing properties and not chemically interacting with gases inserted, Tedlar bags are used to guarantee the physical integrity of the collected samples which will therefore remain uncontaminated and unchanged without changes over time, even during storage.

The analyses of the collected samples are carried out by SPME-GC/MS technique.

2.2 Experimental tests

The collected plastic samples consist of waste tires, 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 2 lists the three experimental tests carried out in this study.

The pyrolysis process operates approximately between 400-420 °C and a retention 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 experimental campaign explained in the previous paragraph is used for investigating the operating parameters in terms of temperature and pressure suitable for the pyrolysis process of the studied samples.

During the #1 of the three scheduled tests 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 below.

In Figure 2(a) the temperatures of the eight thermocouples installed are depicted.

The evolution of the temperature measured at the chimney explains the heating process of the pyrolytic cavity. Indeed, in the first part the temperature of the cavity is set approximately to 400 °C and remains constant for 15' until a lower is defined and maintained constant until the end of the experimental test.

Consequently, the temperatures measured by the three thermocouples installed into the internal chamber grow up to 400 °C and remain constant until the end. The curve named syngas input shows the temperature of the syngas at its exit from the internal cavity. This temperature remains lower than 100 °C and then gradually grows when the syngas starts to flow out.

The #2 experimental test is conducted by introducing waste plastic bags into the inner cavity. During this test the input material was inserted into the pyrolytic reactor following a preheating of the cavity. In particular, the plastic bags are introduced inside the cavity once the same had been heated up to 100 °C.

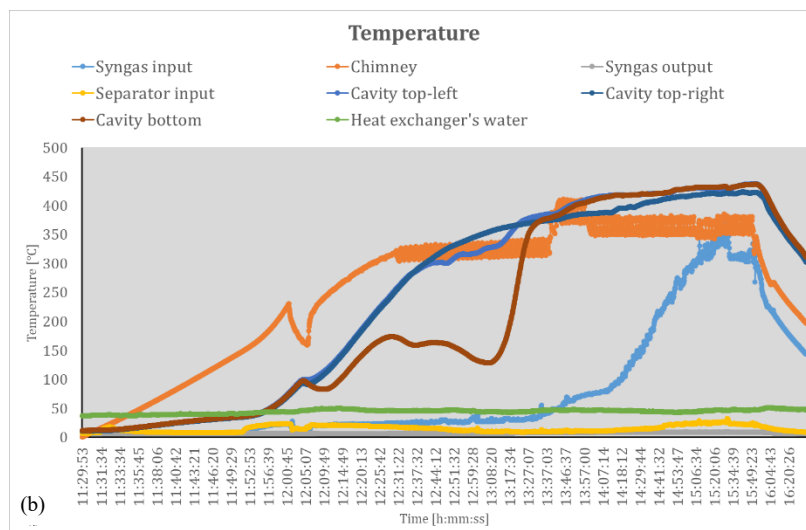
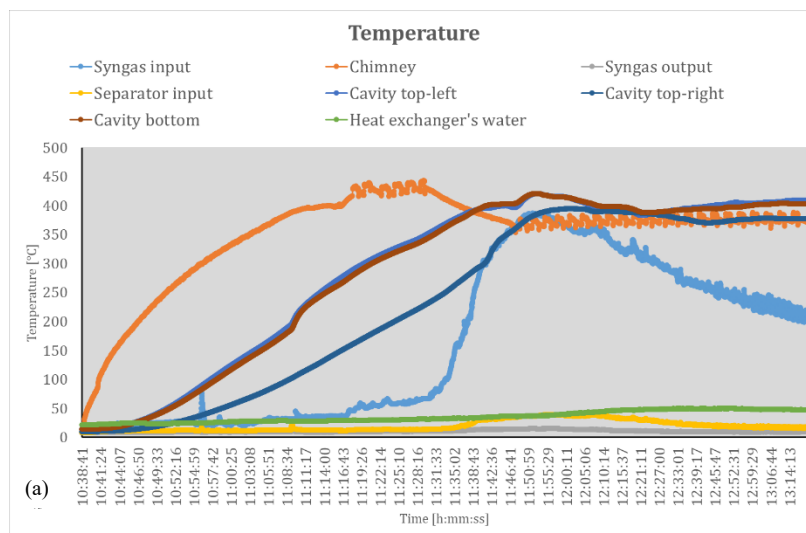
The trend of the temperatures recorded during the test is shown in Figure 2(b).

Thanks to the temperature history represented in Figure 2(b), it is possible to reconstruct the entire development of the experimental test. For a period of time the pyrolytic reactor was kept at a constant temperature of about 350 °C which is then raised by a hundred degrees in order to allow the complete development of the process. In the final section you can see the first phase of shutdown and cooling of the pilot plant with the consequent reduction of all temperatures.

The #3 experimental test 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 2(c).

After a first heating part of the pyrolytic reactor, the last one is kept at a constant temperature to facilitate the transformation of all the materials loaded. As can be seen from Figure 2(c), the increase in temperature measured at the syngas input coincides with the beginning of the formation phase of the syngas.

Figure 2(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.



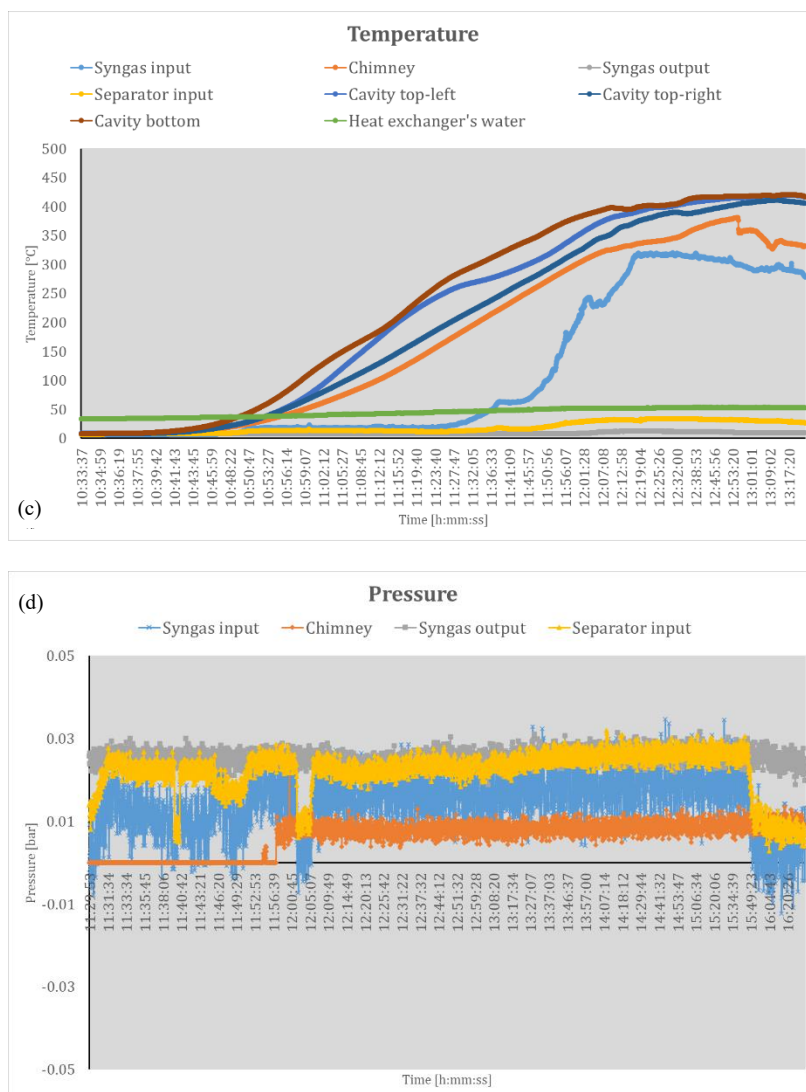


Fig. 2. (a) Waste tires pyrolysis temperatures graph, (b) Polyethylene bags pyrolysis temperatures graph, (c) Rubberized fabric and vulcanized pipes waste pyrolysis temperatures graph, (d) Polyethylene bags pyrolysis pressures graph

3.2 Yields

The effect of different plastic waste types on pyrolysis product yields is shown in Figure 3. All types of plastic waste are degraded at the pyrolysis temperature of 400-420° C.

At the end of the #1 experimental test, as a result of the pyrolytic process, into the internal chamber of the reactor 16 kg (46% wt) of char and 5 kg (14% wt) of steel belts (used to reinforce SUV tires) remain on its bottom. From the separator 12 kg (36% wt) of raw fuel oil are collected (condensation temperature = 45°C). 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. By means of a simple subtraction it is possible to calculate exactly the amount of syngas generated by the pyrolytic process and burned by the torch: 1.5 kg (4% wt).

Thermal pyrolysis of grocery bags (PE) during the #2 test produced relatively less amounts of liquid oil (26%) and char (9%) along with high yield of gases (65%). Unlike the waste tires, which produce a significant amount of fuel oil, the polyethylene bags are transformed for most into syngas.

Results of the last (#3) experimental test into the internal chamber can be resumed as: 4.5 kg (21% wt) of char and 3 kg (14% wt) of steel fibers (used to reinforce pipes and fabrics). Into the separator 9 kg (42% wt) of raw fuel oil are collected. Finally, the amount of syngas generated by the pyrolytic process and burned by the torch can be estimated into 5.2 kg (23% wt).

The average LPG consumption to power the furnace burner is approximately 7 kg per each experimental test.

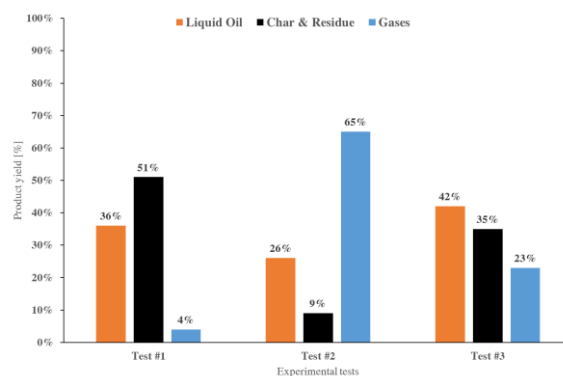


Fig. 3. Effect of plastic waste types on product yields

3.3 Composition

Before considering the composition of the syngas in each experimental test, it is necessary to clarify that the volumetric composition presented into the three tables below is a mean value extracted from the measurements operated by the industrial analyzer.

Table 3. Volumetric syngas composition

Test #	O ₂	N ₂	H ₂	CO	CO ₂	CH ₄	Total
1	1	-	48	10	19	22	100
2	0.2	6	35.4	24	17.3	12.1	92
3	1	-	25	9	28	32	95

In Table 3 the composition of the syngas related to the three experimental tests is presented. Usually the gas-phase products from the pyrolysis of waste tires generally are paraffins (that were clearly visible on the bottom surface of the pipes), olefins, hydrogen, carbon oxides and other small number of other compounds. The H₂ and CH₄ occupied most of the volumetric composition unlike CO₂ and O₂ that represent either the 20% of the total volume of the syngas. Result of this particular volumetric composition the syngas extracted from waste tires has a high-calorific power.

Unlike the previous case related to the pyrolysis of waste tires, the volumetric composition of the pyrogas related to the #2 experimental test varies slightly. Indeed, the percentages of CH₄ and H₂ are reduced as well as those related to CO and CO₂ are increased. Moreover, the syngas relative to the pyrolysis of polyethylene bags is also characterized by minimum

percentages of N₂. Consequently, in this case the calorific value will be reduced compared to the previous one due to the different concentrations found. The remaining percentage points to get to 100% are relative to other components that the industrial analyzer is not able to determine.

Finally, the composition of the pyrogas obtained in #3 shows that the H₂ and CH₄ occupied most of the volumetric composition and CO and O₂ represent the 10% of the total volume of the syngas.

The analysis of the collected samples carried out by SPME-GC / MS technique are presented in the figure below. In this section, only the analyses related to the samples of syngas and exhaust fumes regarding the #2 experimental test (PE bags). Indeed, this case turned out to be the most interesting concerning the quantity of gas that can be extracted from the plastic waste.

Figure 4 shows the chromatograms obtained for the two samples and a blank (the fiber after thermal cleaning). As can be seen from the figure below, the two samples show chromatographic profiles very close to each other following an interesting trend between 13 and 20 minutes. Moreover, in the same interval of time, long chain heterocycles and esters have been mainly detected. The syngas sample shows the same chromatographic profile as the exhaust gases ones but a further characteristic peaks between 1 and 6.5min can be also detected though less intense than the previous ones.

Table 4 shows the list of the analytes detected between 1-6.5 min identified by match with NIST 2014 library.

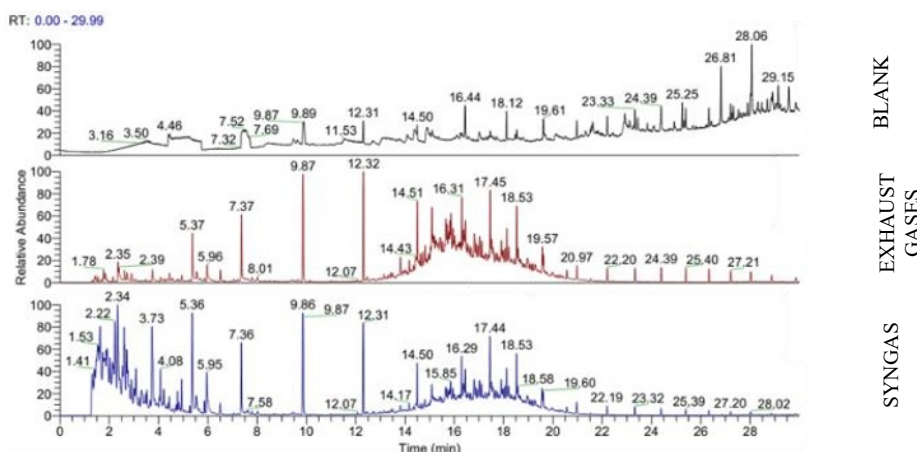


Fig. 4. Chromatograms of the blank and of the two analyzed samples.

Table 4. List of analytes in the 1-6.5 min interval.

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

4 Conclusions

In this paper a fixed plastic pyrolytic reactor prototype has been developed and implemented. The experimental test rig includes the heat exchanger, gas / liquid separator, the torch, and the exhaust treatment system.

The experimental test rig is equipped with specific sensors for the real time acquisition of the main variables of the pyrolysis process: in particular, temperatures and pressures in the main area of the system are registered by means of the LABView interface software.

An experimental campaign has been conducted testing three different samples of PSW: Waste tyres, grocery bags and fabric and rubberized pipes.

The percentages of the output products were monitored and compared with those already present in literature and a good agreement between the two was found.

The percentages of each compound/element constituting the syngas were analyzed in real time thanks to the industrial analyzer and values in line with those found in literature were obtained.

Finally, the composition of the syngas and the exhaust gases for the #2 test, i.e. grocery bags, was investigated by means of SPME-GC/MS technique.

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